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EFFECTS OF TEMPERATURE AND NON-AQUEOUS SOLVENT CHANGES ON SILVER DITHIZONATE EXTRACTIONS

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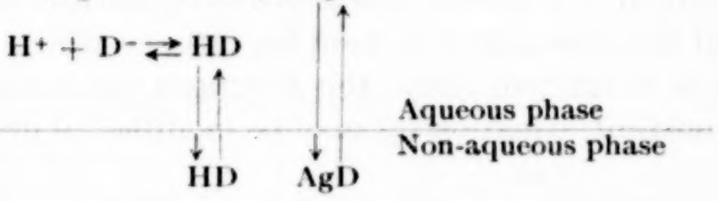
INTRODUCTION

Recently SCHWEITZER AND DYER[1] treated quite extensively the solvent extraction of silver dithizonate from aqueous solutions containing hydrogen ion and anions which mask the extraction of silver into chloroform and carbon tetrachloride. It was found possible to predict the effect of the masking agents, and predictions were made by calculating the pH of the aqueous phase at which 50% of the silver had extracted, $\mathrm{pH}_{\frac{1}{2}}$.

The equation used to predict the $\mathrm{pH}_{\frac{1}{2}}$ of these extractions was based on the following assumed equilibria:

$$\mathrm{AgX_3^{-2}} + \mathrm{X^-} \rightleftarrows \mathrm{AgX_4^{-3}}$$
$$\mathrm{AgX_2^{-}} + \mathrm{X^-} \rightleftarrows \mathrm{AgX_3^{-2}}$$
$$\mathrm{AgX} + \mathrm{X^-} \rightleftarrows \mathrm{AgX_2^{-}}$$
$$\mathrm{Ag^+} + \mathrm{X^-} \rightleftarrows \mathrm{AgX}$$
$$\mathrm{Ag^+} + \mathrm{D^-} \rightleftarrows \mathrm{AgD}$$



where X⁻ represents a specie in the aqueous phase which complexes with and masks the extraction of the silver ion, HD represents dithizone which ionizes in the aqueous phase to give the dithizonate ion D⁻ and hydrogen ion, and AgD represents the monobasic form of silver dithizonate. The complexes between Ag⁺ and X⁻ were called the masking complexes by SCHWEITZER AND DYER[1]. The pH of the aqueous phase which gives 50% extraction was given[1] as

$$\mathrm{pH}_{\frac{1}{2}} = -\log(\mathrm{HD})_o - \log K + \log F \qquad (1)$$

where $(\mathrm{HD})_o$ is the molar concentration of dithizone in the non-aqueous phase, K is the extraction constant for the over-all extraction equilibrium, and F represents a summation term containing the stability constants of the masking complexes. The extraction constant is given by

$$K = \frac{(\mathrm{AgD})_o(\mathrm{H}^+)_w}{(\mathrm{Ag}^+)_w(\mathrm{HD})_o} \tag{2}$$

where the subscripts *o* and *w* refer to the non-aqueous and aqueous phases respectively. The summation term may may be written as

$$F = \sum_{i=0}^{i=4} K_i(\mathrm{X})_w^i \tag{3}$$

where K_i is the stability constant of the *i*th masking complex. K_o is taken as being unity. Equation (1) may be obtained as a special case from the more extensive relations developed by Rydberg[2] and Irving, Rossotti and Williams[3]. In the absence of masking agent the extraction constant may be written as

$$K = \frac{E(\mathrm{H}^+)_w}{(\mathrm{HD})_o} \tag{4}$$

where *E* is the extractability for the system defined as the ratio of the concentration of metal in the non-aqueous phase to the concentration of metal in the aqueous phase.

Schweitzer and Honaker[4] gave for non-masked extractions the equation

$$\frac{(\mathrm{H}^+)_w^n}{(\mathrm{H}^{+\prime})_w^n} = \frac{(S_r'/S_r)^n}{S_c'/S_c} \tag{5}$$

relating at equal extractabilities for two extractions into different non-aqueous solvents the hydrogen ion concentrations in the aqueous phase to the solubilities of the complexing agent and metal complex in the non-aqueous phase expressed as S_r and S_c respectively. The primed and unprimed quantities refer to different non-aqueous solvents, and the exponent *n* is used for cases in which a metal ion with a positive charge of *n* is extracted. Since the hydrogen ion concentration is related to the extraction constant, equation (5) may be modified to give

$$\frac{KS_r^n}{S_c} = \frac{K'S_r'^n}{S_c'} \tag{6}$$

It would appear then that for any number of extractions in which only the organic solvent is allowed to change the equation

$$\frac{KS_r^n}{S_c} = C \tag{7}$$

where *C* is a constant, should be valid. For extractions of silver dithizonate S_r and S_c represent the molar solubilities of dithizone and silver dithizonate respectively in the non-aqueous phase. In this report the constant *C* will be referred to as the solvent factor.

THE SYSTEM

For this research silver was chosen as the metal ion, dithizone as the complexing agent, and several non-aqueous solvents were used. The effects of two variables on the extraction were investigated. The variation of the extraction constant was studied as a function of temperature for extractions from aqueous solutions containing 1.0 M perchloric acid into chloroform and carbon tetrachloride containing dithizone. Extractions were made from 0.1 M potassium bromide solutions into the non-aqueous solvents dichloromethane, chloroform, carbon tetrachloride, benzene, chlorobenzene, bromobenzene, and toluene in order to calculate values of the extraction constant for these extractions. The consistancy of equation (7) was tested for some of the above named solvents from the values of the extraction constants and values for the solubility of dithizone and silver dithizonate in the solvents. In all extractions the concentration of silver ion in the original aqueous phase was approximately 10^{-7} M.

RESULTS AND INTERPRETATION

The effect of temperature

The results obtained for the effect of temperature change on extractions into chloroform and carbon tetrachloride are shown in Table I. Extractions into chloroform were carried out at intervals of 5° from 25° to 55°. Extractions into carbon tetrachloride were carried out at 30°, 35°, 45°, and 55°. In all except one of the extractions the concentration of dithizone in the non-aqueous phase was $1 \cdot 10^{-5}$ M. The concentration of perchloric acid in the aqueous phase was 1.0 M. Linear relations were found to exist between the logarithms of the extraction constants and the reciprocal of the absolute temperature. For extractions into chloroform the equation

$$\log K = 3.5 \times 10^{-3}T^{-1} - 5.9 \quad (8)$$

was obtained. For extractions into carbon tetrachloride the equation

$$\log K = 5.3 \times 10^{-3}T^{-1} - 11.0 \quad (9)$$

TABLE I

RESULTS OF TEMPERATURE CHANGES EXTRACTIONS[a]

Non-aqueous phase	*t°C*	*log K*
Chloroform	25	5.9
Chloroform	30	5.8
Chloroform	35	5.5
Chloroform	40	5.3
Chloroform	45	5.0
Chloroform	50	4.9
Chloroform	55	4.8
Carbon tetrachloride	30	6.5[b]
Carbon tetrachloride	35	6.3
Carbon tetrachloride	45	5.8
Carbon tetrachloride	55	5.3

[a] In all cases but one the initial concentration of dithizone in the non-aqueous phase was $1 \cdot 10^{-5}$ M.

[b] The value of log K for extractions into carbon tetrachloride and chloroform at 30° was reported by SCHWEITZER AND DYER[1].

was found to apply. Equations (8) and (9) are applicable between 25° and 55°. Presumably extrapolations could be made outside this temperature range using these relations. Equation (9) has been used to calculate a value for log K of 7.2 for extractions into carbon tetrachloride at 18°. This result compares well with the value of 7.6 which was obtained by TREMILLON[5].

From equations (8) and (9) it is possible to obtain values of the standard free energy, enthalpy and entropy for the extractions. For extractions into chloroform the values of the free energy, enthalpy and entropy were found to be —8.0 kcal/mole, —16 kcal/mole, and —30 e. u. respectively. Corresponding calculations for extractions into carbon tetrachloride gave —8.0 kcal/mole, —24 kcal/mole, and —50 e. u. for the free energy, enthalpy, and entropy respectively. These thermodynamic functions were found to be nearly constant over the temperature range investigated.

The effect of non-aqueous solvent

The results obtained for extractions into various non-aqueous solvents are shown in Table II. Equation (1) was used to calculate the extraction constant for these extractions. Extractions were made from 0.1 M potassium bromide solutions into non-aqueous solvents containing dithizone which was initially $5 \cdot 10^{-5}$ M. Values of the stability constants for the complexes formed between the silver ion and bromide ions were taken from the work of BERNE AND LEDEN[6]. These constants were used to calculate a value of F for use in equation (1). The solubilities of dithizone were taken from the work of SCHWEITZER AND HONAKER[4]. The solubilities of silver dithizonate were measured by a radio-tracer technique. The object of this part of the study was to test the consistancy of equation (7). Calculated values for the solvent factor, C, which are shown in Table II are seen to be fairly constant for the five solvents for which the solvent factor was calculated. Cyclohexane was tried as a non-aqueous solvent in one extraction. It was found that silver dithizonate is so insoluble in cyclohexane that it produced no coloration of the cyclohexane. Although silver dithizonate was found to be soluble in carbon disulfide little or no silver could be found in the aqueous or non-aqueous phases when extraction experiments were tried. The silver, probably in the form of silver dithizonate, appeared to be adsorbed on some interface in the system.

TABLE II

RESULTS OF NON-AQUEOUS SOLVENT CHANGES ON EXTRACTIONS[a]

Non-aqueous phase	$K \cdot 10^{-6}$	$C \cdot 10^{-6}$	*Solubility (moles/l)* $\cdot 10^{2}$	
			HD	*AgD*
Dichloromethane	1	4	4.9	1.2
Chloroform	0.6	3	7.9	1.6
Carbon tetrachloride	3	2	0.29	0.37
Benzene	2	3	1.4	0.82
Chlorobenzene	3	4	0.98	0.74
Bromobenzene	3			1.1
Toluene	2			0.46
Carbon disulfide				1.1

[a] All measurements were made at 30° from aqueous solutions containing potassium bromide at a concentration of 0.1 M into the non-aqueous solutions which were initially $5 \cdot 10^{-5}$ M with dithizone.

EXPERIMENTAL CONDITIONS

Extraction studies, chemicals, apparatus and technique

The chemicals, their preparation and purification, the apparatus used, and the techniques employed in the extraction studies were the same as used previously by SCHWEITZER AND DYER[1].

Solubility measurements, chemicals, apparatus and technique

The solubility of silver dithizonate in various non-aqueous solvents was measured by the use of radio-active silver dithizonate containing ^{110}Ag. More than enough silver dithizonate to saturate 5 ml of the non-aqueous solvent was placed in a 25-ml glass stoppered Erlenmeyer flask. Five ml of the non-aqueous solvent was added along with a magnetic stirring bar. The flasks were stoppered, placed in the constant temperature bath, and stirred for five hours. The solutions were then sampled by withdrawing a 0.1-ml sample through a cone of filter paper into a micropipette. The sample was placed on a planchet, allowed to dry, and counted with a Tracerlab 1000 Scaler using a G-M tube. By counting a 0.1-ml sample from a solution of the radio-active silver dithizonate of a known concentration, it was possible to obtain the unknown concentrations of the saturated solutions. The solution of known concentration was prepared by weighing a quantity of the silver dithizonate, placing it in a volumetric flask, and diluting with chloroform to the capacity of the flask.

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SUMMARY

The extraction of 10^{-7} *M* silver ion from aqueous solutions into non-aqueous solvents containing dithizone has been investigated. The effects caused by changing the temperature and non-aqueous solvent were studied. Values of the extraction constant for extractions into chloroform and carbon tetrachloride were obtained as a function of temperature. Plots of the logarithm of the constants *versus* the reciprocal of the absolute temperature were straight lines. A linear relation was found between the extraction constant and the ratio of the solubilities of silver dithizonate and dithizone in the non-aqueous solvent. This relation was found to hold for extractions in which the non-aqueous phase was dichloromethane, chloroform, carbon tetrachloride, benzene and chlorobenzene.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction de l'argent dans des solvants non-aqueux renfermant de la dithizone. Ils ont examiné l'influence de la température et de divers solvants.

ZUSAMMENFASSUNG

Es wird eine Untersuchung beschrieben über die Extraktion von Silber mit nicht-wässrigen Lösungsmitteln in Gegenwart von Dithizon und der Einfluss von Temperaturänderungen und anderen Lösungsmittel geprüft.

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DETERMINATION OF METAL CYANIDE AND THIOCYANATE COMPLEXES BY KJELDAHL-GUNNING AND CARIUS SEALED TUBE DIGESTION METHODS

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A variety of methods have been reported for the determination of the cyanide ion employing all of the general techniques of analytical chemistry as volumetric[1], spectrophotometric[2], and amperometric[3], to mention only a few. None of these methods are applicable to the determination of cyanides in the inert transition metal complexes. Many investigators have described the determination of metal cyanide complexes. Generally, each method is limited in its application to a specific compound and the iron cyanide complexes have been studied almost exclusively. Some other methods have been attempted for the determination of the cyanide complexes. Chief among these is the evolution method of RUBNER AND BACHKA as applied by BIEG[4]. Although this method is applicable to the inert transition metal complexes it requires much time and the handling of large amounts of distillate.

The chief limitation of the methods developed to date is that they may not be readily applied to the determination of the inert transition metal cyanide and thiocyanate complexes. Carbon analyses of these complexes are generally difficult. The same is true of the Dumas nitrogen determination.

This paper describes methods which are applicable to the determination of metal cyanide complexes using the classical Kjeldahl digestion or Carius combustion followed by a Kjeldahl type of distillation.

The use of the Kjeldahl apparatus has been reported by HORAN AND EPPIG[5] for the determination of ammonia in cobalt penta- and hexa-ammines. The Kjeldahl-Gunning method as described in A.S.T.M. has been used by JUNG AND COPELLO[6] for the analysis of blue pigments. The destruction of ferrocyanide in an autoclave at 130° employing ammonium polysulfide as the reducing agent has been reported by ADELSBERGER[7]. Also, the hydrolysis of cyanides in hydrochloric acid at 140° has been reported by GETTER AND GOLDBAUM[8], followed by a colorimetric determination of ammonia.

The modified Kjeldahl-Gunning method or the combined use of the Carius sealed tube digestion and Kjeldahl distillation enable the analysis of the metal cyanide, thiocyanate and mixed cyanodiphenanthroline complexes with greater ease and accuracy than provided by the existing methods. These procedures are especially applicable to micro analytical techniques and may be applied to for the analysis of metal cyanide, thiocyanate complexes.

EXPERIMENTAL

Reagents and apparatus

Reagent grade concentrated sulfuric acid, $d = 1.84$ was used for the digestion. Decomposition was catalysed by the reagent grade anhydrous mercuric sulfate and mercuric oxide mixture. The receiving flask contained 4% boric acid. Titration was carried out using approximately 0.015 N hydrochloric acid, the normality of which was checked against anhydrous sodium carbonate and ammonium sulfate using methyl red and methylene blue mixed indicator. 50% sodium hydroxide containing 5% thiosulfate was used to neutralize sulfuric acid in a distillation flask. Reagent grade sodium salt of ethylenediaminetetraacetic acid (EDTA) was added to break ammonia complexes of some of the transition metals.

Reagent grade potassium ferro- and ferricyanides, and mercuric thiocyanate were obtained from the Baker and Adamson Co.; potassium cobalticyanide was procured from the G. F. Smith Chemical Co. Sodium aquo-, amminopentacyanoferrates(II) and Reinecke's salt were prepared by the procedure described in the BRAUER's "Handbuch der Präparativen Anorganischen Chemie". Potassium salts of cyanide complexes of chromium(III), manganese(III), nickel(II) and molybdenum(IV) were obtained from G. ATKINSON, and dicyano-bis(1,10-phenanthroline)-iron(II) from A. SCHILT (both from our laboratories). All compounds were analysed for water of crystallization and metal contents.

Kjeldahl distillations were carried out using one piece micro Kjeldahl distillation apparatus.

PROCEDURE

Kjeldahl-Gunning method

The digestion of the transition metal cyanides was carried out essentially by the Kjeldahl-Gunning method. A sample weighing approximately 10 to 25 mg was placed directly from the charging tube into the micro Kjeldahl digestion flask. About 50 mg of mercuric sulfate and mercuric oxide mixture was then added to the digestion flask followed by the addition of 2.0 ml of concentrated sulfuric acid saturated with mercuric oxide. The contents were mixed slowly, and the flasks were placed on a low flame for about 10 min, then digestion was continued for an additional 80 min on full heat. Prolonged digestion caused poor reproducibility and low results. Throughout the digestion period flasks were rotated frequently to ensure complete mixing and to get all the spattered solid sulfates from the walls of the digestion flasks. At the end of the digestion the flasks were cooled. The contents were diluted with approximately 3-4 ml of water. The diluted digest was then transferred to the micro Kjeldahl distillation flask. About 150 mg of sodium salt of ethylenediaminetetraacetic acid (EDTA) was added. (The addition of EDTA was necessary with all the transition metal cations forming inert ammonia complexes). Six ml of 50% sodium hydroxide containing 5% thiosulfate was then added and the distillation was started. Samples were distilled for 7 min. The distillate was collected in 4% boric acid. The ammonia absorbed was titrated with a standard hydrochloric acid using methyl red and methylene blue mixed indicator.

Carius sealed tube method

An alternative Carius sealed tube digestion method was found to be superior (than the Kjeldahl-Gunning procedure). A micro sample was placed into the Carius combustion tube from the charging tube. Mercuric oxide and mercuric sulfate mixture and sulfuric acid were added as in the above procedure. The sealed tubes were placed in the Carius heating furnace. The samples were heated for 2 h at 315°. The tubes were cooled and they were opened taking regular precautions by releasing pressure first. The opened tubes were heated on the micro burner and they were boiled for about

TABLE I

ANALYSIS OF NITROGEN IN METAL CYANIDE AND THIOSULFATE COMPLEXES

Substance analyzed	Method of		% calculated[a]	Ammonia found	Recovery of nitrogen %	Average deviation[b] p.p.t.
	digestion	distillation				
Potassium ferrocyanide	Kjeld.-Gunn.	No EDTA	19.89	20.01	100.6	6
Potassium ferrocyanide	Carius	No EDTA	19.89	19.97	100.4	2
Potassium ferricyanide	Kjeld.-Gunn.	No EDTA	25.51	25.11	98.43	7
Potassium ferricyanide	Carius	No EDTA	25.51	25.34	99.33	5
Sodium ammonopentacyanoferrate(II)	Kjeld.-Gunn.	No EDTA	24.56	24.36	99.18	5
Sodium ammonopentacyanoferrate(II)	Carius	No EDTA	24.56	24.50	99.75	4
Sodium aquopentacyanoferrate(II)[c]	Kjeld.-Gunn.	No EDTA	21.41	21.63	101.0	9
Sodium aquopentacyanoferrate(II)[c]	Carius	No EDTA	21.41	21.52	100.5	5
Dicyano-bis(1,10-phenanthroline)-iron(II)	Kjeld.-Gunn.	No EDTA	5.98	11.30[d]	188.9	30
Dicyano-bis(1,10-phenanthroline)-iron(II)	Carius	No EDTA	5.98	6.03	100.8	5
Tetrapyridinodithiocyanato-iron(II)	Kjeld.-Gunn.	No EDTA	5.74	9.57[e]	166.7	100
Tetrapyridinodithiocyanato-iron(II)	Carius	No EDTA	5.74	8.32[e]	144.9	100
Potassium hexacyanochromate(III)	Kjeld.-Gunn.	EDTA added	24.46	24.58	100.5	11
Potassium hexacyanochromate(III)	Carius	EDTA added	24.46	24.42	99.83	4
Potassium hexacyanocobaltate(III)	Kjeld.-Gunn.	EDTA added	25.28	24.85	98.30	9
Potassium hexacyanocobaltate(III)	Carius	EDTA added	25.28	25.13	99.40	2
Potassium hexacyanomanganate(III)	Kjeld.-Gunn.	No EDTA	24.90	24.79	99.56	9
Potassium hexacyanomanganate(III)	Carius	No EDTA	24.90	24.97	100.3	4
Potassium octacyanomolybdate(IV)	Kjeld.-Gunn.	No EDTA	22.56	22.55	99.95	5
Potassium octacyanomolybdate(IV)	Carius	No EDTA	22.56	22.51	99.78	4
Potassium tetracyanonickelate(II)	Kjeld.-Gunn.	EDTA added	20.92	20.95	100.1	5
Potassium tetracyanonickelate(II)	Carius	EDTA added	20.92	20.95	100.1	5
Ammonium diammonotetrathiocyanatochromate(III)	Kjeld.-Gunn.	EDTA added	27.65	27.64	99.96	
Ammonium diammonotetrathiocyanatochromate(III)	Carius	EDTA added	27.65	27.63	99.93	3
Dithiocyanatomercury(II)	Kjeld.-Gunn.	No EDTA	8.84	8.77	99.20	5
Dithiocyanatomercury(II)	Carius	No EDTA	8.84	8.82	99.77	3

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[a] Calculated values are based on the results of the analyses rather than expected formula weights.

[b] Average deviation in p.p.t. is based at least on five determinations.

[c] Sodium aquopentacyanoferrate(II) contains sodium ferrocyanide and sodium nitroprusside as impurities.

[d] Some of the phenanthroline is decomposed during the digestion. Results depend on the digestion conditions.

[e] Some pyridine is distilled and the results vary with the time of distillation.

4 min until sulfur dioxide fumes were expelled. The digest was then diluted with water and the contents were transferred to the distillation flask.

RESULTS AND DISCUSSION

In concentrated sulfuric acid and in presence of mercuric ion as a catalyst conversion of metal cyanide complexes to ammonium sulfate proceeds rather rapidly. However, quantitative recovery of nitrogen as ammonia is greatly dependent upon the digestion conditions. Thus, Kjeldahl-Gunning and Carius sealed tube digestion methods have been investigated to a greater extent. The results of the analyses of metal cyanide, thiocyanate and ammonia complexes are summarized in Table I.

The phenanthroline–cyanide complexes yield high and irreproducible results when using the Kjeldahl-Gunning digestion method. Apparently, phenanthroline is decomposed somewhat under these conditions. In the Carius sealed tube digestion phenanthroline is not attacked and the cyanide is hydrolyzed to ammonia exclusively. The mixed complexes of pyridine–thiocyanate or cyanide cannot be analyzed by these methods. Pyridine is distilled with ammonia, and the results depend upon the time of distillation. The somewhat low results for the potassium ferricyanide are attributed to the absorption of water on the powdered sample.

Recovery of nitrogen as ammonia after the digestion by Kjeldahl-Gunning method is in the order of 99%. The results obtained are mostly low and there is a considerable scattering of the values. This is probably due to the loss of nitrogen during the digestion as has been observed by SELF[9] and CARPIAUX[10] when the final digest is a solid. Indeed, metal cyanide complexes during digestion yield insoluble sulfates. Reproducibility becomes poorer if the digestion has been extended over 3 h. In general, 90 min time of digestion is sufficient to decompose metal cyanide and thiocyanate complexes.

In the Carius sealed tube digestion method recoveries are better than 99% and the scattering of the results is less than in the Kjeldahl-Gunning method. The digestion temperature should be high enough to decompose cyanide and thiocyanate complexes and not too high to shatter the tubes. At 250° only about 90% of the cyanide is converted to ammonia; thiocyanates are not effected at this temperature. At 315° all of the metal cyanide and thiocyanate complexes studied are converted to ammonia quantitatively.

The conversion of cyanide to ammonia in the Kjeldahl-Gunning method is also greatly effected by the amount of water present in the original digest. The results are low by a few per cent and not reproducible if the sulfuric acid concentration falls below 15 *M*. At lower concentrations of sulfuric acid the recovery of ammonia becomes poorer. This is probably due to the loss of hydrocyanic acid. The evolution of cyanide as hydrocyanic acid has been used for the determination of cyanide by the Liebig method.

SUMMARY

Small amounts of metal cyanide and thiocyanate complexes can be determined using either the Kjeldahl-Gunning or Carius sealed tube digestion method. The results obtained by the Kjeldahl-Gunning method are somewhat low and the values are scattered. The Carius sealed tube digestion enables analysis not only of metal cyanide and thiocyanate but also of mixed phenanthroline–cyanide complexes. The results are reproducible and more accurate than in the Kjeldahl-Gunning method.

RÉSUMÉ

Les auteurs ont examiné le dosage des complexes métalliques cyanés et thiocyanés, soit par la méthode de Kjeldahl-Gunning, soit par la méthode en tube scellé de Carius. C'est cette dernière qui a donné les résultats les meilleurs. Elle permet en outre l'analyse de complexes mixtes phénanthroline-cyanure.

ZUSAMMENFASSUNG

Die Bestimmung von komplexen Metallcyaniden und thiocyanaten kann entweder nach der Kjeldahl-Gunning oder Carius Methode erfolgen. Die Kjeldahl-Gunning Methode ergibt etwas zu tiefe und streuende Werte. Die Carius Methode gibt bessere Werte und kann ausserdem auch für Phenanthrolin-Cyanid Komplexgemische angewandt werden.

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FURTHER APPLICATIONS OF ELECTRO-STATIC DISCHARGE CURRENT (ES. D.)

VII. A MOISTURE GAUGE FOR CHROMATOGRAPHS

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The importance of moisture in determining the conductance of chromatograph zones which contain soluble compounds is well known. By placing the chromatograph in a "humidiser" prior to zone location the writer showed[1] that the conductivity of an otherwise almost undetectable zone or spot could be located and underlined automatically.

The correct length of exposure to moisture in the "humidiser" varies in accordance with the humidity of the atmosphere. Automatic underlining is possible over a comparatively wide range of humidity, from a degree where there is only just sufficient moisture to permit reliable operation to the point where the chromatograph becomes oversaturated.

The simple device described in the present paper is a gauge whereby the gradual conditioning of the chromatograph can be monitored until it reaches the most favourable condition.

The electrical circuit

As shown in Fig. 1, the circuit is virtually the same as that employed[2] in a previous paper except that the conductimetric tube is now replaced by the "humidity gauge" F. The latter consists of a strip of No. 1. Whatman's filter-paper which has been soaked in $N/1$ cobalt chloride or another hygroscopic solute. When dry it is mounted in front of back plate 'B', Fig. 2. To ensure good contact, that portion which is covered by the washers between which it is clamped, is coated with graphite.

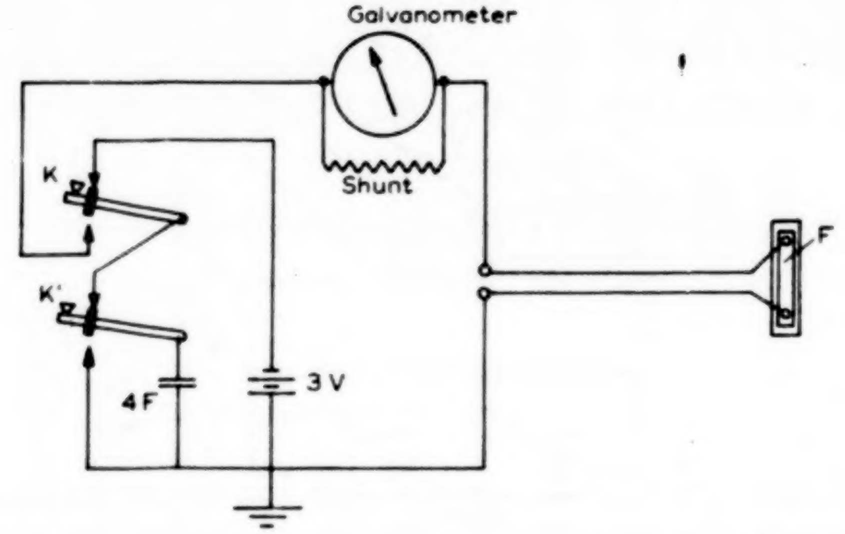

Fig. 1. The electrical circuit employed with BLAKE's humidity gauge.

There is an air space between the strip and the plate. The humidity gauge is then placed at the end of the humidiser and is shut in under its glass cover. From time to time key K* (Fig. 1) is depressed and galvanometer swings are recorded covering the humidity range within which automatic recording can be relied upon. A swing 'X' is found a short distance past the centre of this range and an indicator is attached to the galvanometer scale at that point.

To ensure reliable automatic operation the galvanometer swing must always reach the neighbourhood of the indicator.

Procedure for using the humidity gauge

Normally the gauge is suspended at some convenient place in proximity to the automatic zone locating apparatus. While it is still out in the open air and before it is placed in the humidiser a preliminary test is made. Key 'K' is depressed and a galvanometer swing is observed; if this comes well within the operational range *i.e.* close to point X on the scale, the chromatograph which also has been exposed to open air in the laboratory will not require any additional moisture and it can be run through the underlining apparatus as it is. However if the galvanometer swing falls short of the indicator on the scale, the chromatograph is too dry and the procedure is then as follows:

The gauge is placed inside the humidiser in the position indicated by A, Fig. 2. The chromatograph is then placed above it and along the groove in the usual manner. The humidiser is then sealed by its glass cover.

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* The functions of the two keys K and K' were described[2].

Key 'K' is then depressed every 15 sec or so until the required swing 'X' occurs. At this juncture the chromatograph is properly conditioned and underlining should be commenced.

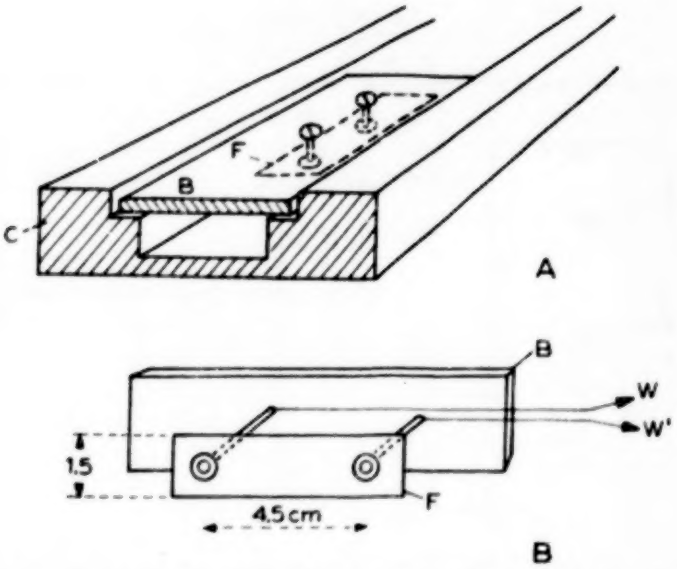

Fig. 2. A. This drawing shows the end-view of the "humidiser". The humidity gauge is seen in position where it rests along the top groove. B. This figure illustrates the general arrangement of the humidity gauge. F is the strip of filter-paper impregnated with cobalt chloride.

Originally the gauge was designed for use with the automatic apparatus; but it is of course equally applicable in the case of a hand operated locator.

An alternative scheme

Instead of impregnating the filter-paper strip with a hygroscopic substance, the writer has found that a similar strip of clean filter-paper (which itself is slightly hygroscopic) can be employed as a "humidity gauge" provided that the condenser is charged to a sufficiently high potential, 67.5 V gave satisfactory galvanometer swings.

SUMMARY

This paper describes a simple "humidity gauge" whereby the degree of humidity of a chromatograph is monitored both before and during its conditioning. Originally it was designed for use in conjunction with BLAKE's automatic zone locator. It can also be employed with a hand operated zone locator.

RÉSUMÉ

L'auteur décrit un dispositif permettant de contrôler le degré d'humidité d'un chromatographe, soit avant, soit au cours de son exécution.

ZUSAMMENFASSUNG

Es wird eine Einrichting beschrieben, die erlaubt, den Feuchtigkeitsgehalt in einer chromatographischen Kammer sowohl vor als auch während des Betriebes zu messen.

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A NEW GAS ABSORPTION DEVICE

ITS APPLICATION TO TITRIMETRIC AND CONDUCTOMETRIC MICRO DETERMINATIONS OF CARBON DIOXIDE IN AIR

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The starting point for the present study was the widely used method for the titrimetric determination of carbon dioxide in atmospheric air developed by **Krogh and Rehberg**[1] and slightly modified by **Fonselius, Koreleff and Buch**[2]. In this method, a measured volume of atmospheric air (50 to 100 ml) is passed at a low flow rate (approximately 10 ml per minute) upwards through an oblique glass tube of diameter 0.4 to 0.5 cm and length about 15 cm. The bottom end of this tube is tapered and bent upwards, and the upper end is provided with a bulb with a diameter of about 1.5 cm (Fig. 1). In this tube is previously introduced 0.5 ml of a dilute solution of barium hydroxide. During the absorption the tilt of the tube should be adjusted so that droplets of the fluid separate the air bubbles of the ascending air stream until they reach the bulb where they break up, starting a counter stream of fluid flowing towards the bottom end of the tube in a layer wetting the inner surface of the tube. The liquid of the ascending droplets mixes with and stirs the descending liquid. The excess of hydroxide is finally titrated with hydrochloric acid.

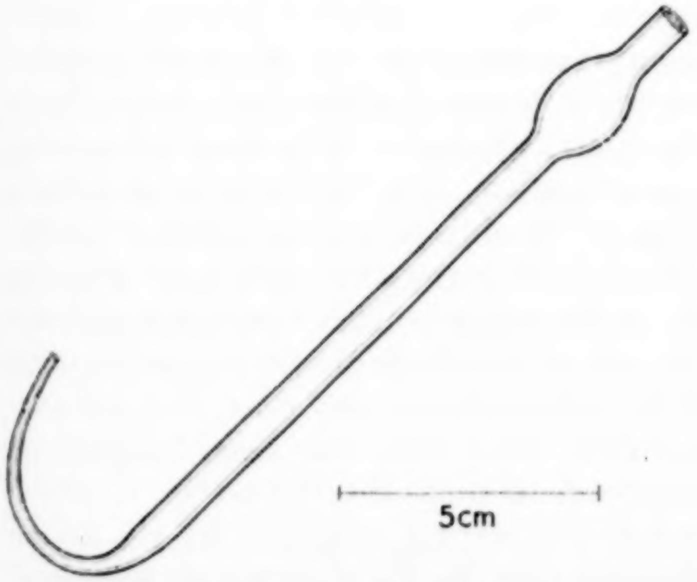

Fig. 1. The absorption tube of **Krogh and Rehberg**.

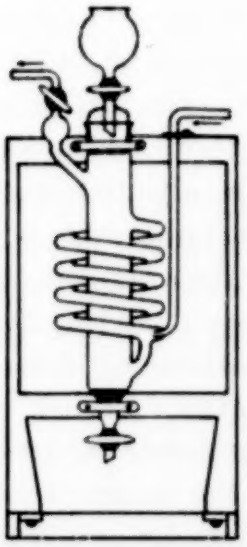

Fig. 2. The spiral absorber of **Weaver and Edwards**. With gas flowing at a rate of 100 ml per min the bubbles are stated to remain in the helix about 7 sec.

During an experimental study in which a great number of determinations of carbon dioxide in air had to be carried out, the writer considered the possibility of simplifying the procedure of KROGH AND REHBERG by carrying out the analyses as simple titrations of the barium hydroxide solution with air, thus avoiding the back titration of the surplus of hydroxide. In these experiments the absorption liquid was 0.5 ml of a 0.005 N barium hydroxide solution. Thymolphthalein, previously added to the barium hydroxide solution, was used as indicator.

It was found that the error involved in this technique corresponded to a loss of carbon dioxide which, for the same absorption tube and the same flow rate of the air, was quite accurately reproducible. Apparently, the error decreased with the flow rate. With air streams of 12, 7 and 2 ml per minute, the losses of carbon dioxide were found to be about 20, 8, and 4%, respectively. In consequence, more complete absorption of the carbon dioxide was attempted by increasing the length of the absorption tube. Experiments with a long tube of the same internal diameter, 0.42 cm, revealed that by very careful adjustment of the tilt of the tube, the ascending droplets of fluid could be made to travel about 60 cm before they broke up; they could travel only about 12 cm in the original KROGH AND REHBERG tube. By this arrangement, the area of contact between air and liquid and (for the same rate of flow) the duration of the contact are both increased by a factor of about five.

With air streams of 13, 5.5 and 2 ml per minute, the apparent escape of carbon dioxide was now found to be about 6 to 10, 1 to 4, and —3 to +1%, respectively. It was noticed that the colour change of the indicator in this modified tube, contrary to that in the original KROGH AND REHBERG tube, did not occur simultaneously in all the ascending droplets, but always started at the bottom end of the tube when about 85% of the air volume required to change the colour of the entire amount of hydroxide had passed. During the final period of the absorption, the colour change would gradually spread upwards through the entire volume of the absorbing liquid. This means that the absorbing area of contact between air and hydroxide towards the end of the absorption represented only a fraction of the total wetted inner surface of the tube.

From the above experiments it was concluded that more efficient absorption might be obtained if the recirculation of the absorption fluid from the top to the bottom of the tube could be improved. An absorption device was therefore made which combined the principal advantages of the above absorption tube (large absorbing surface and favourable ratio between the absorbing area and the volume of absorbing fluid) with the effective mixing and stirring of the absorption liquid offered by the so-called spiral absorbers originally described by WEAVER AND EDWARDS[3] (Fig. 2). These spiral absorbers also operate on the air lift principle. They have been used for many purposes including the collection of carbon dioxide from a stream of air with subsequent titrimetric determinations of the carbon dioxide absorbed (MARTIN AND GREEN[4], PIETERS[5], BLOM AND EDELHAUSEN[6]). They have also been adapted to conductometric determinations of carbon dioxide (DAILLY AND ELLIOT[7]).

However, the quantities of carbon dioxide required for analyses with the above spiral absorbers are much larger than those required by the KROGH AND REHBERG procedure, because 10 to 50 ml of absorption liquid are needed as against 0.5 ml in the KROGH AND REHBERG method. Furthermore, the ratio between the area of the absorbing surface and the volume of absorbing liquid in these spiral absorbers is less favourable, being of the order of 1 cm² per ml of liquid as against about 30 cm² per ml in the original KROGH AND REHBERG tube, and more than 100 cm² per ml in the modified KROGH AND REHBERG tube described above.

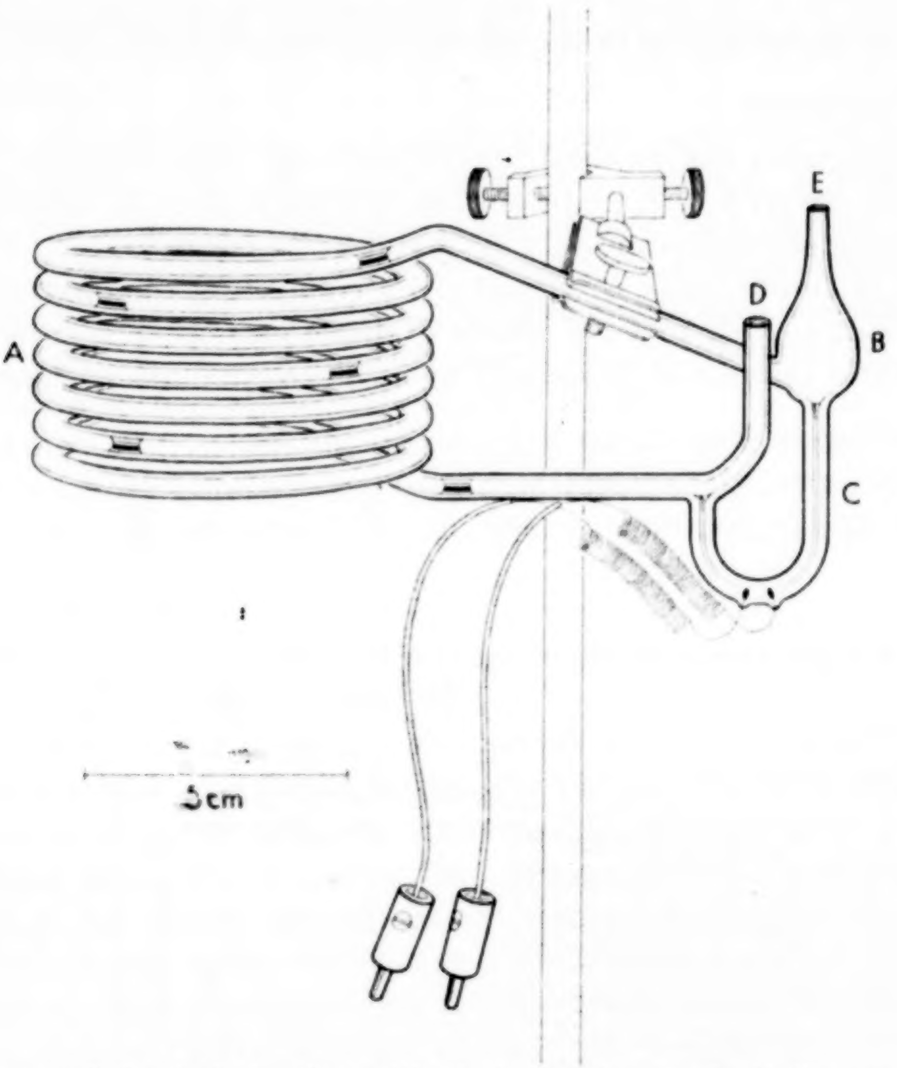

Fig. 3. The recommended spiral absorber with electrodes for conductivity measurements. For explanation, see text.

Fig. 3 shows the proposed absorption device in its final form which was reached after many experiments. Containing 0.5 ml of absorbing liquid, it gives a ratio between the area of the absorbing surface and the volume of the absorbing liquid of about 300 cm² per ml. The apparatus is made entirely of glass, "Pyrex" or "Jena Geräte". It consists of a spiral tube (A), the upper end of which ends in a flattened bulb (B), the bottom of which is connected to the lower end of the spiral through a capillary tube (C). The lower bend of (C) is provided with electrodes for conductivity measurements. D is the inlet tube for the air to be analyzed. E is the outlet tube.

Dimensions of apparatus

Spiral tube (A), length 160 cm, internal diameter 0.32 cm ± 0.02 cm; diameter of the helix (5 to) 7 cm; volume about 13 ml; internal surface area about 160 cm².

Bulb (B), horizontal outer diameters about 1.4 cm and 0.8 cm, respectively; volume about 1 ml.

Capillary tube (C), internal diameter 0.065 cm ± 0.005 cm. The difference between the levels of the upper and lower ends of this capillary tube is 1.9 cm ± 0.2 cm. At the lower bend the tube is slightly blown up to accommodate the platinum electrodes. The volume of the capillary tube is less than 0.05 ml.

Electrodes, consisting of platinum wires, 0.04 cm in diameter, are melted into the lower bend of the capillary tube. The ends protruding into the bore of the tube are flattened; the areas are a few mm². The distance between the electrodes is about 0.4 cm.

Inlet tube (D), internal diameter 0.32 cm. The part adjacent to the lower end of the capillary tube (C) is narrowed to a bore of about 0.26 cm.

Outlet tube (E), length about 1.2 cm; internal diameter about 0.2 cm.

The volume of air contained in the whole apparatus is about 15 ml.

Preparation of apparatus

Before the apparatus can be used for conductivity measurements the electrodes should be lightly covered with platinum black. This is done as follows: 0.1 ml of a solution containing chloroplatinic acid (3%) and lead acetate (0.02%) is placed in the apparatus and platinum black is deposited by connecting the electrodes through a resistance of about 1000 Ω to a 4-V source of direct current. The current is reversed every 15 sec. Three periods of 15 seconds in each direction are sufficient.

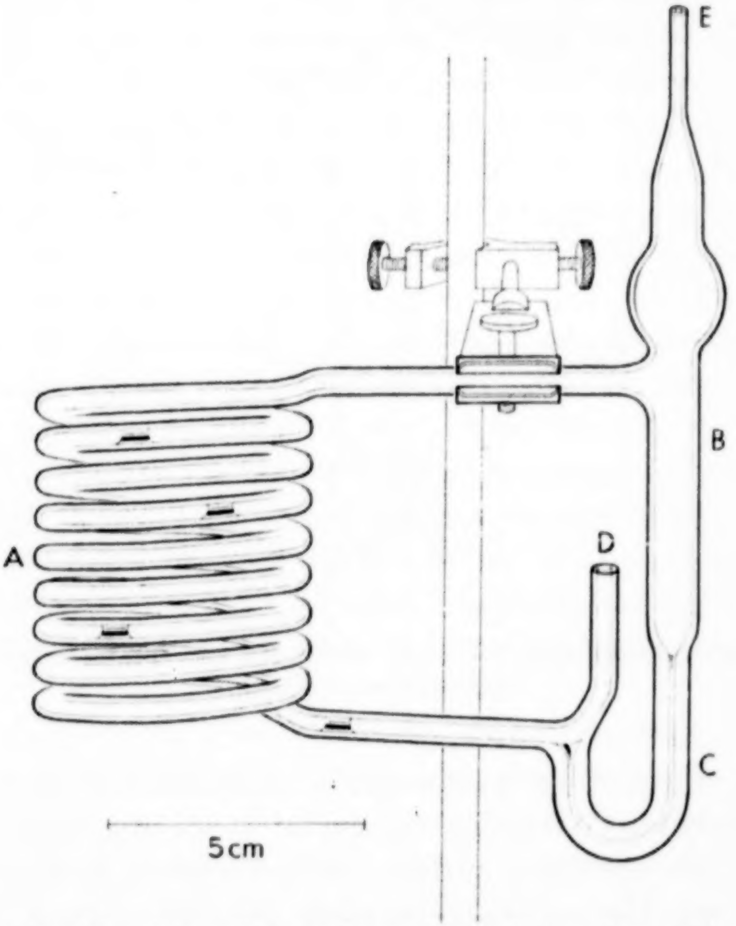

Fig. 4. A more primitive form of the proposed spiral absorber, without electrodes.

Fig. 4 shows a spiral absorber which may be preferred for certain purposes; a volume of absorption fluid up to about 2 ml can be circulated at a rate of up to about 20 ml per minute. It has a larger dead space than the absorber described above, and this is a disadvantage for many purposes.

The experiments discussed below were carried out with the spiral absorber shown in Fig. 3.

Before the apparatus is used for the first time, it is rinsed successively with approximately N hydrochloric acid, distilled water and alcohol. A water pump is connected to the outlet tube (E) and the washing fluid is introduced through the inlet tube (D). After the washing, the spiral is turned upside down and allowed to dry in the air stream before the suction pump is disconnected. The absorber is then ready for use.

The absorber is washed between each analysis with distilled water and alcohol only. The adhering precipitates of barium or strontium carbonate need only be removed occasionally by washing with hydrochloric acid.

Absorption solution

For both the visual titrimetric and conductometric analyses, the same solution is used for the absorption of carbon dioxide. Strontium hydroxide is preferred to barium hydroxide because strontium carbonate is less soluble than barium carbonate. For most purposes, 0.005 M strontium hydroxide, saturated with strontium carbonate and containing 10 ml of an alcoholic 0.1% thymolphthalein solution per litre was used. For precise analyses, this solution should be standardized by titration with standard hydrochloric acid at intervals of a few days.

By means of a KROGH syringe pipette 0.5 ml of the absorption solution is delivered into the inlet tube of the spiral absorber, which is immediately connected to the tubing delivering the air to be analyzed. The analysis is then carried out without delay.

End-point determination

The end-point of the visual titration is taken as the disappearance of the last traces of the blue colour of thymolphthalein.

The conductometric measurements are carried out with a very convenient and inexpensive commercial Wheatstone bridge, the Philips Measuring Bridge P.R. 9500. The measurements are performed with an alternating current of 1000 cycles per second from an oscillator incorporated in the bridge. The margin of error of this instrument is not significant to the present study and will not be discussed in this paper.

The electrodes of the spiral absorber can be calibrated with a freshly prepared 0.01 M potassium chloride solution, the specific conductivity of which at t° can be taken as $\varkappa_t = [1333 + 27(t - 22)] \cdot 10^{-6}$ Ohms^{-1} cm^{-1}. The electrode constant K is then computed from the equation

$$\varkappa_t = \frac{K}{R_t}$$

where R_t is the resistance in Ohms measured at t°. For the electrodes of the spiral absorbers, K should not exceed 15. In most of the absorbers K was about 13. K is not sufficiently constant to allow the initial concentration of strontium hydroxide in the absorbing liquid to be checked accurately from measurements of the specific conductivity. However, K does not change measurably during the performance of a single analysis.

In the determinations of carbon dioxide, it was found convenient to express the results of the conductivity measurements as the ratio between the conductance measured and the initial conductance of the absorption liquid, which is equal to R_0/R, where R_0 is the initial resistance of the absorption liquid and R the resistance measured.

Testing the apparatus

Before the spiral absorbers are used for the analyses, it should be ascertained that the absorption fluid circulates properly. The outlet tube of the absorber to be tested is connected to a Mariotte bottle as described below and the rate of air flow adjusted to about 12–15 ml per minute. By means of a measuring syringe, the absorption liquid is introduced in quantities of 0.1 ml through the inlet tube while the circulation of the fluid is watched.

The first 0.1 ml of fluid should fill the capillary tube and also yield a drop of fluid which travels with the air stream through the spiral. This drop is gradually reduced in size as it leaves a layer of fluid adhering to the wall of the spiral, and after having passed less than one third up the spiral tube it breaks up. The second quantity of 0.1 ml should start a drop travelling about two-thirds of the spiral before it breaks. The third quantity of 0.1 ml should complete the circuit and separate from the air in the bulb without splashing into the outlet tube; the fluid should return to the lower end of the spiral through the capillary tube without catching air bubbles in this tube. The spiral absorber should be able to function with 0.3 ml of fluid but only one or two droplets of fluid then travel simultaneously in it. By the addition of further liquid, the number of circulating droplets should increase. In most of the spirals, more than 1 ml of fluid may circulate without the accumulation of appreciable quantities in bulb B.

The spiral absorber is then disconnected, washed and dried as described above and again connected to the Mariotte bottle.

In the next test, a quantity of 0.5 ml of the absorption solution is delivered into the inlet tube before the air stream is started. The whole quantity of fluid apart from a small fraction filling the capillary starts to travel through the spiral forming an unbroken string of fluid. When it reaches the bulb, it should again be noticed if the fluid separates from the air without spraying into the outlet tube. Owing to the retardation caused by the capillary tube, the fluid entering the spiral for the second circulation should separate into at least two single drops, and in subsequent circuits the number of droplets should be at least five.

If the above test is repeated with 0.7 or 1.0 ml of absorbing liquid, the number of circulating droplets is further increased. However, only a few spirals with the dimensions given above for the absorber shown in Fig. 3 can circulate as much as 1 ml of fluid at a rate corresponding to an air-flow of 15 ml per minute without the permanent accumulation of fluid in the bulb. In the analyses discussed below, no permanent accumulation of fluid in the bulb was allowed.

Among about twenty of these absorbers tested, only one had to be discarded because it, for some reason, constantly trapped air bubbles in the capillary tube, so that the recirculation of the fluid was blocked. In two absorbers, the same fault was overcome by decreasing the distance between the levels of the upper and lower end of the capillary tube by 0.2 cm.

The principal errors to be expected in carrying out determinations of carbon dioxide in air with this absorber may be grouped as follows:

1. Errors caused by the exchange of carbon dioxide through the wall of the flexible tubing leading the sample stream of air to the inlet tube of the absorber.

2. Errors caused by the liberation of substances from glass into the absorption liquid and by adsorption and sorption to the glass of ions from the liquid, as well as errors due to exchange of ions between liquid and glass.

3. A positive error due to the absorption of part of the carbon dioxide in the air initially present in the apparatus.

4. A negative error due to incomplete absorption of carbon dioxide from the sample air stream.

To elucidate the significance of these errors a number of experiments were carried out. Samples of air with different concentrations of carbon dioxide were used.

a. Carbon dioxide-free air was obtained by passing ordinary air at a constant rate (about 30 ml per minute) by means of a small membrane pump first through a tower filled with soda lime and then through a wash-bottle containing distilled water. The following measures sufficed to minimize any errors caused by diffusion of carbon dioxide through the walls of the flexible tubing joining the tower, the wash bottle and the spiral absorber (*cf.* the errors in group 1 above): (1) only "Tygun" tubing, which is known to be far less permeable to carbon dioxide than rubber tubing, was used; (2) one cm from the end of the tubing leading to the inlet of the absorber a T-glass joint was interposed, the side branch of which was fitted with 30 cm of flexible tubing for the escape of surplus air. In this way, the effect of diffusion of carbon dioxide through the flexible tubing on the carbon dioxide concentration of the air entering the absorber was made independent of the air-flow through the spiral; in all experiments this was less than 20 ml per minute. When carbon dioxide-free air was used to wash the absorber before an experiment, the tubing attached to the side branch of the T-tube was closed by a stopper.

b. Atmospheric air was sampled through a 2-m long "Tygun" tube from the outdoor atmosphere. A T-glass joint was again interposed 1 cm from the inlet of the absorber. The side-arm was connected to a suction pump for washing the tube with atmospheric air before the air was passed through the absorber. Continuous washing during the absorption procedure proved unnecessary.

c. Air containing carbon dioxide in different concentrations. In some experiments these mixtures were stored in a Douglas bag. Owing to the solubility of carbon dioxide in rubber, the carbon dioxide concentration of these samples changed continuously.

During the experiments carried out with these qualities of air, the sample air was drawn through the absorber at different rates. This was established by connecting the outlet tube (E) of the absorber to a Mariotte bottle, from which the water could be drained through different capillary tubes. The volume of air passed was taken to be equal to the volume of water delivered by the bottle.

In all experiments discussed below, the fluctuation of the temperature measured by a thermometer suspended adjacent to the spirals was less than ±0.2° during periods of 10 minutes, and less than ±0.4° in 30 minutes; no correction for the effect of temperature changes on the conductivity were made.

Errors caused by the liberation of substances from the glass, by adsorption and sorption to the glass, and by exchange of ions between liquid and glass were studied by the following experiments with carbon dioxide-free air.

A clean dry absorber was connected as described above to the apparatus delivering carbon dioxide-free air. The T-joint in this experiment was connected to the inlet tube of the absorber by 2 cm of rubber tubing. In order to avoid any back-diffusion of carbon dioxide from the ambient air, the outlet tube of the absorber was provided with a 30-cm length of "Tygun" tubing. After washing with the carbon dioxide-free air for 10 minutes the outlet tubing was connected to the Mariotte bottle; 0.5 ml of the standard strontium hydroxide solution was injected by means of a KROGH measuring syringe provided with a fine needle through the short rubber connection into the inlet tube of the absorber. The initial resistance of the absorption solution, R_0, was measured, and a stream of carbon dioxide-free air of about 10 ml per minute was started by opening the outflow tube of the Mariotte bottle. The resistance, R, between the electrodes was then measured at intervals over a period of several hours.

An initial, instantaneous decrease in conductivity of 3.5% was found and this was followed by a steady decrease in the conductivity of about 4% per hour. On repeated runs, the initial drop of conductivity was invariably found to be between 2.5 and 4%; it could not be reduced even when the period of washing with carbon dioxide-free air was extended to several hours. The same initial drop occurred when the experiment was repeated with different absorbers, of which some were made of "Pyrex" glass and others of "Jena Geräte" glass. The steady loss, however, varied between 2 and 6% per hour, apparently being higher in experiments with new absorbers than with those which had been used for days or weeks. This steady loss could not be reduced by interposing a scrubber with sodium hydroxide solution between the soda lime tower and the water-filled scrubber; moreover, the decrease per hour was independent of the rate of the air stream which was varied between 1 and about 15 ml per min. It was found, however, that raising the temperature of the absorber greatly increased the rate of the continuous decrement of the conductivity. At about 55°, the conductivity of the usual strontium hydroxide solution decreased by about 20% of the initial conductivity at 55° during the first hour. When the spiral was then cooled to room temperature (22°), the rate of the decrease returned to its usual magnitude of 4% of the initial conductivity at 22° during the following hour.

From these observations it was concluded that the changes in the conductivity of the absorption fluid were not caused by contamination of the so-called carbon dioxide-free air with carbon dioxide, but should be explained as the results of reactions between the absorption fluid and the glass.

The initial drop in the conductivity of the absorption liquid of 3.5% corresponds to the disappearance from the solution of $3.5/100 \times 2.5$ μmoles = approx. 0.09 μmoles of strontium hydroxide. If this quantity of strontium hydroxide were adsorbed on the glass surface, it would (on the assumption that it forms a monolayer of cubical, closely packed molecules) cover a surface of 80 cm^2, *i.e.* about 50% of the internal surface of the spiral. Therefore, it seems not unlikely that the initial drop in the conductivity of the strontium hydroxide solution may be caused by adsorption of strontium hydroxide on the surface of the glass spiral.

In view of the results of the above experiments, the continuous decrease in conductivity must also be ascribed to interactions between the strontium hydroxide solution and the glass, possibly a steady liberation of silica from the glass.

These experiments were supplemented by some in which three spiral absorbers were connected in series. "Tygun" tubing and glass tubes were used except for short lengths of 2 cm of rubber tubing adjacent to the inlet tubes of the spiral absorbers. After the clean and dry absorbers had been washed with carbon dioxide-free air, the usual quantity of strontium hydroxide solution was added to the inlet tubes of the first and the third absorber by injection through the rubber tubing. After about 1 hour, the same quantity of strontium hydroxide was injected into the inlet tube of the second spiral absorber. Immediately after the injections, the usual initial drop in conductivity invariably occurred in each absorber.

Similar experiments were carried out with more dilute solutions of strontium hydroxide prepared by exposing the above 0.005 *M* solution to atmospheric air. The strontium hydroxide concentrations of these solutions were determined by conductivity measurements. With these solutions, the initial drop in conductivity expressed as above, *i.e.*, as a percentage of the initial conductivity of the hydroxide solution used for the experiment, was larger; however, the decrement was found to be smaller than that corresponding to the disappearance of the same quantity of strontium hydroxide. The initial drop in the conductivity of 0.002 *M* strontium hydroxide solutions was found to be about 5%; thus the quantity of presumably adsorbed strontium hydroxide was only about two-thirds of that found with undiluted strontium hydroxide solution.

A still more dilute ($4 \cdot 10^{-4}$ *M*) solution showed an initial decrement of conductivity of about 10%; *i.e.* the absorption was about one-fourth of the amount with the undiluted solution. With a 0.015 *M* strontium hydroxide solution, the initial drop in the conductivity was 1.3% of the initial conductivity of this solution; *i.e.* the same quantity of strontium hydroxide was absorbed as with the 0.005 *M* solution.

Any error arising from the absorption of part of the carbon dioxide present in the air contained in the apparatus at the beginning of the analysis was studied in similar experiments in which the spiral absorbers were washed with air with different concentrations of carbon dioxide before the introduction of the usual quantity of 0.005 *M* strontium hydroxide solution. Then carbon dioxide-free air was passed through the absorber and the initial drop in conductivity was determined. The difference between this drop and the above-mentioned initial drop of 3.5% (due to adsorption) was assumed to be caused by the absorption in the hydroxide of carbon dioxide from the air originally present in the spiral.

With fresh atmospheric air this difference amounted to about 1% of the initial conductivity of the usual strontium hydroxide solution; this corresponds to the carbon dioxide contained in about 2 ml of fresh atmospheric air, and this volume is about 13% of the total volume of air contained in the absorber. With air streams ranging from 2 to 15 ml per minute that part of the initial drop in conductivity caused by the absorption of carbon dioxide from the air originally present in the apparatus seemed to be independent of the flow rate. The quantity of carbon dioxide absorbed was further found to be roughly proportional to the square root of the concentration of carbon dioxide in the air originally contained in the apparatus.

With these experimental data, it is possible to consider experiments for elucidating the significance of the error caused by incomplete absorption of carbon dioxide under various experimental conditions.

In the first experiments to be discussed, carbon dioxide was liberated from a mixture of sulphuric acid and measured quantities of a very carefully prepared solution of 0.005 *M* sodium bicarbonate. By means of a stream of carbon dioxide-free air the carbon dioxide was carried through two successive spiral absorbers with strontium hydroxide; the conductivities were measured.

These experiments were carried out with three absorbers connected in series with short lengths of rubber tubing interposed in the connecting tubings adjacent to the inlet tubes of the absorbers as described on page 19. In the first absorber (No. 0), which had previously been rinsed with hydrochloric acid, washed and dried as described on page 16, was introduced 0.5 ml of 0.1 *N* sulphuric acid. After washing with a stream of carbon dioxide-free air, about 10 ml per minute, for 30 minutes, 0.5000 ml of the usual strontium hydroxide solution was injected through the walls of the rubber tubing into each of the other two absorbers (Nos. 1 and 2). After a further 30 to 120 min, a measured quantity of the sodium bicarbonate solution was injected into absorber No. 0.

The first experiments with this arrangement were carried out with 0.5000 ml of the bicarbonate solution. The quantity of carbon dioxide liberated, 2.50 μmoles, was equivalent to the absorption capacity of the strontium hydroxide present in each of the subsequent spiral absorbers; conductivity measurements showed that 88% was absorbed in No. 1 and 12% in No. 2. This poor result was assumed to be due to the very sudden transference of the carbon dioxide in a too concentrated mixture with air. Consequently, the experiment was repeated with a glass bulb (volume about 25 ml) interposed in the tubing between the absorber in which the carbon dioxide was liberated and the absorber containing strontium hydroxide.

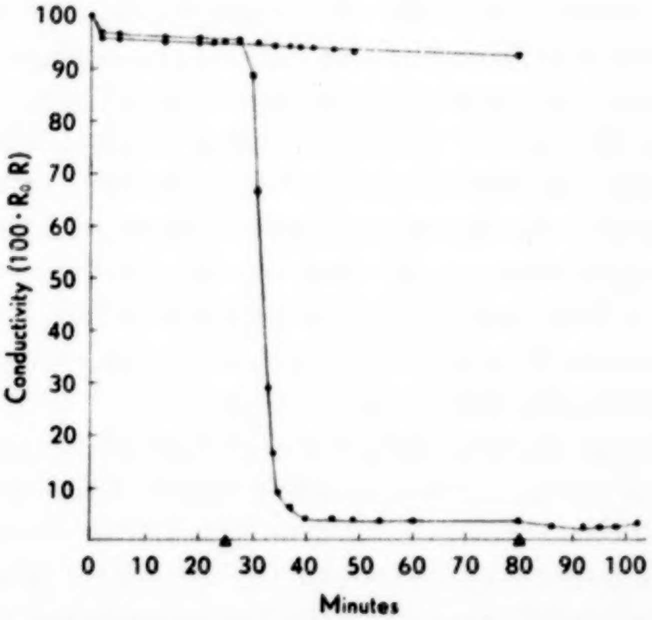

Fig. 5. The conductivities of the absorption liquids of two absorbers connected in series plotted against time; carbon dioxide equivalent to 97% of the capacity of the solution in absorber No. 1 was carried through the absorbers by means of carbon dioxide-free air. The carbon dioxide was liberated after 25 min. After 80 min the air stream was changed to fresh atmospheric air.

The results of this experiment are given in Fig. 5, in which the conductivities of the absorption fluids of the two spiral absorbers, expressed as percentages of the initial conductivities, are plotted against time, measured in minutes after the introduction of the hydroxide to the absorbers. The flow-rate of the carbon dioxide-free air was 8.33 ml per min. By titration, the concentration of strontium hydroxide in the absorbent was found to be 0.00515 M. Thus, the quantity of strontium hydroxide, 0.500 ml, in each spiral absorber was 3.0% in excess of the amount equivalent to the carbon dioxide liberated.

The conductivity curves exhibited the usual initial drop of about 3.5% (3.0% in absorber No. 1 and 4.0% in absorber No. 2). The subsequent continuous decrement of conductivity during a period of 25 min in which only carbon dioxide-free air was passed was 1.5% in both cases.

After the bicarbonate had been added to the sulphuric acid, the conductivity curve of the strontium hydroxide solution in absorber No. 2 was not affected; the conductivity of the liquid in absorber No. 1 dropped during less than 20 min to a level of 4.0%, and during the next 40 min steadily decreased to 3.5%. During this period the liquid still possessed a faint but clearly visible blue colour. When now fresh atmospheric air was admitted to absorber No. 1, the conductivity of the liquid in it rapidly passed its minimum value of 2.2% of the initial conductivity; at the same time the last traces of the blue colour disappeared. Then a slow but steady increase due to the uptake of carbon dioxide as bicarbonate took place. During the next 10 min the conductivity increased from 2.2 to 2.9%. This experiment was repeated several times with essentially the same results.

Under these experimental conditions there was no measurable escape of carbon dioxide from the solution in absorber No. 1. This means that even towards the end of the absorption process when only a very small surplus of hydroxide is present, the removal of carbon dioxide from a very dilute mixture with carbon dioxide-free air is still complete.

After the absorption of 2.50 μmoles of carbon dioxide in a quantity of strontium hydroxide equivalent to 103% of the carbon dioxide, and 1 hour after the strontium hydroxide had been placed in the absorber, there remained an excess of hydroxide of about 1.3%; this leaves 1.7% of the initial strontium hydroxide to have been removed by interaction with the glass. It is reasonable to assume that this 1.7% corresponds to the continuous drop of conductivity of the absorption liquid mentioned above; the initial drop of about 3.5% must be due to reversible processes, probably adsorption, (*cf.* page 20) and, consequently, cannot affect the amount of carbon dioxide which can be taken up by the hydroxide solution.

In further experiments the amount of strontium hydroxide placed in absorber No. 1 minus the amount corresponding to the continuous decrement of the conductivity before the delivery of the bicarbonate, was equivalent to the amount of bicarbonate placed in absorber No. 0; the escape of carbon dioxide from absorber No. 1 was then determined to be about 1% from conductivity measurements in absorber No. 2. In these experiments in which the absorption of the last few per cent of carbon dioxide took place from a very dilute air mixture, the rate of the air stream did not measurably influence the amount of carbon dioxide escaping absorption.

The next experiments were carried out with air streams, whose carbon dioxide concentrations were constant throughout each experiment. They were intended to correlate the quantity of carbon dioxide escaping absorption (1) to the rate of the air stream and (2) to the concentration of carbon dioxide in the sample air. These experiments were also carried out with three absorbers connected in series as described on page 19. After washing with carbon dioxide-free air as described above, 0.5 ml of the strontium hydroxide solution was injected in each absorber and carbon dioxide-free air at about 10 ml per min was passed for 30 to 120 minutes. The stream of the sample air was then turned on, and the conductivity was measured in each of the three absorbers at suitable intervals until the indicator had changed colour in all three spirals.

The results of a representative experiment carried out with a stream of atmospheric air of 8.33 ml per min are shown in Fig. 6. It can be seen that the conductivity of the absorption fluid in each of the first two absorbers had attained its minimum level before the conductivity measured in the subsequent absorber was affected by more than about 1%. However, it is not justifiable to conclude that there had been practically no escape of carbon dioxide from the absorbers during the last few minutes before the minimum conductivity was reached. The volume of air contained in each spiral plus the volume of the preceding interconnecting tubing was about 17 ml; as the rate of the air stream was 8.33 ml per min, the registration by the conductivity measurement of the carbon dioxide escaping from the preceding absorber must have been delayed by more than 2 min.

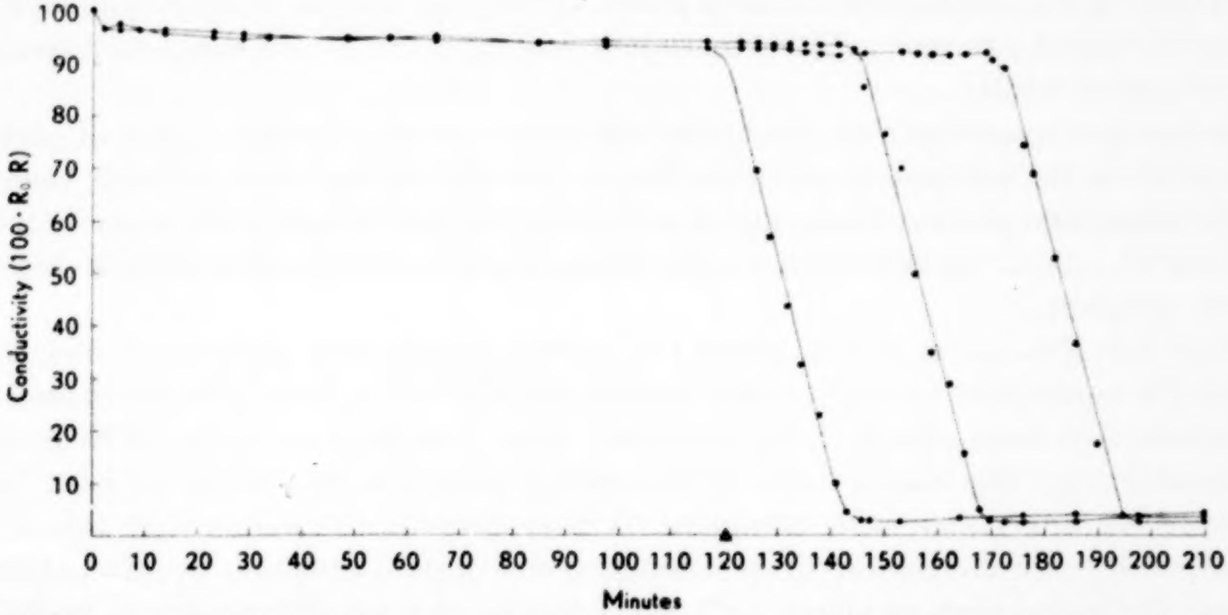

Fig. 6. The conductivities of the absorption liquids in three absorbers in series plotted against time. After 120 minutes the stream of carbon dioxide-free air was changed to atmospheric air at a rate of 8.3 ml per min.

In order to measure the escape of carbon dioxide towards the end of the titration in analyses carried out on atmospheric air the following procedure was adopted. Three spiral absorbers were connected in series as described above except that a three-way stopcock was interposed between the inlet tube of the first absorber and the tubings delivering atmospheric air and carbon dioxide-free air. By this arrangement it was possible to make instantaneous changes between the streams of the two airs. The spiral absorbers were washed with carbon dioxide-free air before the usual quantity of strontium hydroxide was placed in each absorber. Carbon dioxide-free air was then passed for about 30 min in order to establish the slope of the conductivity curves caused by the interactions between the absorption fluid and glass. The air stream was then changed to atmospheric air. As soon as the colour had changed in the first absorber, the air stream was changed to carbon dioxide-free air; the quantity of carbon dioxide which had passed through the first absorber, was determined from the drop of the conductivity curve of the fluid in the subsequent absorber during the passage of a further 50 ml of carbon dioxide-free air, allowance being made for the continuous decrement of the conductivity due to interaction between the absorption fluid and the glass. The steady slope of the conductivity curve of the solution in the third absorber was only used as an indicator of temperature constancy during the experiments.

The amount of carbon dioxide escaping absorption in the first absorber, expressed as a percentage of the amount absorbed in this absorber, may, with sufficient accuracy, be considered equal to the drop in the conductivity of the solution in the second absorber expressed as a percentage of the initial conductivity of this solution; this amount is denoted as Δ. The percentage of the total quantity of carbon dioxide absorbed in the first plus the second absorber that has escaped the first absorber is then $(100 \times \Delta)/(100 + \Delta)$.

The first experiments were carried out with atmospheric air. This air stream was changed to carbon dioxide-free air when the last traces of the blue colour of thymolphthalein had disappeared. With air streams of 15, 8.3 and 2.2 ml per min, Δ was found to be about 6 to 8, 4 to 6, and 1 to 2%, respectively.

The next experiments were carried out with air streams of 15 and 8.33 ml per min; these rates were changed to 2 ml per minute as soon as the blue colour of the absorption liquid began to fade. The escape of carbon dioxide (Δ) was then found to be 3 to 6 and 2 to 4%, respectively.

In further experiments it was found that the above escape of carbon dioxide could not be significantly decreased by reducing the rate of the air stream below 2 ml per min whenever the first fading of the blue colour was noticed. However, it appeared that the amount of carbon dioxide escaping from the first absorber towards the end of the titration could always be reduced to less than 3% of the absorption capacity of the 0.5 ml of 0.005 M strontium hydroxide in this absorber if, whenever the first fading of the colour of the absorbent occurred, the stream of air was changed to an alternating passage of 40 ml of carbon dioxide-free air and 2 ml of atmospheric air. (Compare the results obtained with carbon dioxide liberated from bicarbonate and acid described on pages 21–22; these show that absorption of very low concentrations of carbon dioxide from air is nearly complete even just before the end-point of the titration is reached.)

Concerning the above-mentioned findings it should be noted that the escape of carbon dioxide is caused not only by its incomplete absorption while the fluid is still more alkaline than corresponds to the disappearance of the last colour of thymolphthalein (pH = 9.4); it must also be partly due to the unavoidable introduction of a surplus of carbon dioxide with the air stream, when, towards the end of the titration, only a small quantity of alkali is left.

If the average pH of the absorption liquid is assumed to be 10.4 when the first drop of the absorbent fades, the concentration of strontium hydroxide is $1.25 \cdot 10^{-4}$ M, or 2.5% of its initial concentration. The quantity of carbon dioxide which can be taken up as carbonate by this solution corresponds to the carbon dioxide contained in less than 5 ml of atmospheric air; this is only one-third of the volume contained in the spiral absorber.

These experiments with atmospheric air were repeated with samples of air containing lower concentrations of carbon dioxide (about 0.01 and 0.003%). The escape of carbon dioxide towards the end of the titration was found to decrease with decreasing concentrations of carbon dioxide. With air containing 0.01% of carbon dioxide, the escape of carbon dioxide from air streams of up to 12 ml per min was always below 2%. If the rate of this air stream was reduced to less than 5 ml per min as soon as the colour of the indicator began to fade, the escape of carbon dioxide was only about 1%.

Repetition of these experiments with air containing carbon dioxide in considerably higher concentrations showed an appreciable increase in the amount of carbon dioxide escaping absorption. With a stream of air containing 0.15% of carbon dioxide, *i.e.* about 5 times the concentration in fresh atmospheric air, the escape, Δ, at a constant flow rate of 8.3 ml per minute was found to be about 45%; this corresponds to an escape of (100 × 45)/145 = 31% of the carbon dioxide content of the air passed through the first absorber. At 2 ml per minute, Δ was found to be 8 to 10%. When the flow rate was changed from 8.3 to 2 ml per min as soon as the first drop of the absorption liquid began to fade, the escape was about 12%. If at the first fading of the colour, the stream of air was changed to an alternating passage of 40 ml of carbon dioxide-free air and 2 ml of atmospheric air, the absorption liquid could be titrated to the end-point indicated by the disappearance of the last trace of the blue colour; the escape of carbon dioxide was then only about 5%.

CONCLUSIONS AND SUGGESTIONS

It seems reasonable to conclude from all these results that the absorption device described is suitable for the determination of carbon dioxide. Probably the spiral absorber could also be used for the determination of other gaseous substances.

The procedures to be recommended for the analyses depend on the accuracy required and the laboratory facilities available. It is beyond the scope of this study to discuss in detail the numerous ways in which the apparatus described can be adapted to different requirements and various experimental conditions. Only a few examples of analytical procedures which have been tested by the writer are outlined here.

1. *Colorimetric titrations of carbon dioxide in air by titration against strontium hydroxide*

0.500 ml of the strontium hydroxide solution is delivered into the open inlet tube of the spiral absorber by means of a KROGH syringe pipette and titrated with a stream of the air to be analyzed to an end-point determined by the complete disappearance of the colour of the first two drops of the circulating absorbing liquid. From the volume of air used for the titration, an empirical correction which is taken to be equal to the volume of air passed in one minute is deducted. The resulting volume is then reduced to dry air at 0° and 760 mm Hg most conveniently by means of a reduction factor read from a thermobarometer. The concentration of carbon dioxide at NTP is calculated by dividing the amount of strontium hydroxide used (about 2.5 μmoles) by the air volume. The carbon dioxide concentration thus obtained is expressed as μmoles CO_2 per ml of air at NTP. Multiplication by 2.24 gives the carbon dioxide concentration in per cent.

Provided that the concentration of carbon dioxide is below 0.1%, the relative error involved in the above procedure does not exceed 5%. The accuracy of the visual titrations may be improved by carrying out the simultaneous analyses of the sample air and air containing a known carbon dioxide concentration. The carbon dioxide concentration of the unknown air sample can be taken to be equal to the ratio between the volumes of the known and the unknown air samples multiplied by the carbon dioxide concentration of the known air. When the difference between the carbon dioxide concentrations of the two samples is small, in practice below 20%, the error is approximately the same as that found when samples of the same air are repeatedly titrated. For atmospheric air, the reproducibility was found to be better than ±2%. This procedure offers the advantage that the exact titre of the strontium hydroxide solution need not be known.

2. *Conductometric methods*

For the analysis of atmospheric air, conductometric procedures do not give results that are essentially more accurate than ±2%. However, the conductometric methods are indispensable for certain purposes, particularly for checking the accuracy of the visual procedures. Furthermore, they can be used for analyses when the visual procedures are unsuitable. The following analyses may be mentioned as examples.

1. Determination of changes occurring in the carbon dioxide concentration in a continuous stream of air.

2. Determination of the carbon dioxide concentration of small samples of air. By means of a stream of carbon dioxide-free air, small air samples can be carried through the spiral absorber and the carbon dioxide determined by measuring the resulting decrease in conductivity. To ascertain that no carbon dioxide has escaped, a second absorber may be connected in series. In this way, accurate determinations of the carbon dioxide content of 1-ml samples of expired air and of carbon dioxide liberated from small volumes of biological fluids by means of sulphuric acid can be carried out. (For technical details, see the experiments described on page 22).

ACKNOWLEDGEMENTS

The writer wishes to thank Professor P. BRANDT REHBERG, University of Copenhagen, for reading the manuscript. He is indebted to Mr. CHORFITZ PETERSEN, glass blower at the University of Aarhus, who very skilfully made the spiral absorbers, and to Mr. PREBEN GROSS, the Zoological Museum, Aarhus, for drawing the figures.

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SUMMARY

A gas absorption device is described which is capable of absorbing gases from a stream of air (up to 15 ml/min) in a small volume (about 0.5 ml) of absorbing fluid. The absorbing area of contact between air and liquid is about 150 cm². The apparatus is provided with electrodes for measuring the electrolytic conductivity of the absorbing liquid. It can be used in the determination of carbon dioxide in air by means of conductometric titrations; visual titrations with air by means of thymolphthalein are also possible. No back-titration of the strontium hydroxide absorbent is needed.

RÉSUMÉ

Un nouvel appareil est décrit pour l'absorption des gaz. Il est pouvu d'électrodes, permettant la mesure de la conductibilité électrolytique du liquide absorbant. Se basant sur des mesures de conductivité, cet appareil a pu être appliqué au dosage de l'anhydride carbonique dans l'air. Il est possible également d'effectuer une détermination colorimétrique, grâce au changement de coloration de la thymolphtaléine, se produisant au point final du titrage.

ZUSAMMENFASSUNG

Es wird ein Absorptionsapparat beschrieben, welcher die Gasen in einem Luftstrom (bis *ca.* 15 ml/min) in etwa 0.5 ml einer Absorptionsflüssigkeit absorbiert. Der Apparat ist mit Elektroden versehen, zur Messung der elektrolytischen Leitfähigkeit der Absorptionsflüssigkeit. Er findet Anwendung zur Bestimmung des Kohlendioxydgehaltes der Luft durch konduktometrische oder kolorimetrische Titration. Rücktitration der angewandten Hydroxide ist nicht erforderlich.

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A SPECTROPHOTOMETRIC METHOD WITH 1,1'-DIANTHRIMIDE FOR THE DETERMINATION OF STRENGTH OF CONCENTRATED SULPHURIC ACID

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INTRODUCTION

The strength of concentrated sulphuric acid is usually determined volumetrically, thermometrically, conductometrically or by density measurement. The conductometric method is widely applied in industry for continuous production control purposes. Owing to the small and irregular variation of density with concentration in the range 90 to 100% sulphuric acid, the measurement of density is less satisfactory in this range.

A spectrophotometric method of determining the concentration of sulphuric acid was introduced by ZIMMERMAN AND BRANDT[1]. These authors plotted absorption curves of quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) dissolved in concentrated sulphuric acids of varying strength and found an isosbestic point at 585 mμ. By measuring the extinctions at certain wavelengths and calculating the ratio of extinction, the concentrations of sulphuric acids in the range 85 to 99% could be determined.

In the present paper 1,1'-dianthrimide is applied in a similar way, the difference being the measurement of extinction at a single wavelength and the use of a constant amount of reagent. The organic reagent 1,1'-dianthrimide is mainly used for spectrophotometric determination of boron, but other elements, such as germanium and tellurium may also be determined. The colour of these complexes is only developed by heating and will not interfere in the present determination.

The reagent was found to be slightly soluble in sulphuric acid of strength below about 65%, but in the range 65 to 100% acid and in fuming acids 1,1'-dianthrimide dissolves readily producing a green-coloured solution. 1,1'-Dianthrimide seemed to exist in at least two modifications. The concentration of the green-coloured modification utilized in this investigation was found to increase with the strength of acid. This observation offers the possibility of determining the strength of sulphuric acid by spectrophotometry, and a method has been worked out for the determination of acids in a concentration range of about 80 to 99%.

Instruments and reagents

Instruments: Extinction measurements were made with a Zeiss spectrophotometer PMQ II and matched 1.0-cm cells.

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Reagents: 1,1′-Dianthrimide, concentrated (95–97%) and fuming (about 20% SO_3) sulphuric acid were of reagent grade quality. The 1,1′-dianthrimide was stored in a desiccator. The strength of the stock solution of sulphuric acid was determined volumetrically and found to be 96.12%.

Standard solutions: The reagent may be added either in the solid state or as a standard solution. The latter was prepared by dissolving 1.000 g of 1,1′-dianthrimide in 100 ml of 96.12% sulphuric acid.

A series of sulphuric acids of known concentration was prepared by adding either distilled water or fuming acid to 96.12% acid. The exact strength of the solutions was determined by titration.

EXPERIMENTAL

Absorption and standard curves

A 10^{-3} *M* solution of 1,1′-dianthrimide in concentrated sulphuric acid showed a broad absorption maximum at about 650 mμ. At wavelengths below 500 mμ the absorption curves rose steeply, and at wavelengths above 700 mμ the extinctions decreased to small values. At 650 mμ and at a constant concentration of 1,1′-dianthrimide the extinction was found to vary with the strength of acid.

In Fig. 1 extinctions are given for two series of acids containing 20 and 80 mg of reagent per 100 ml. The measurements were carried out at 650 mμ against 96.12% acid as blank solution.

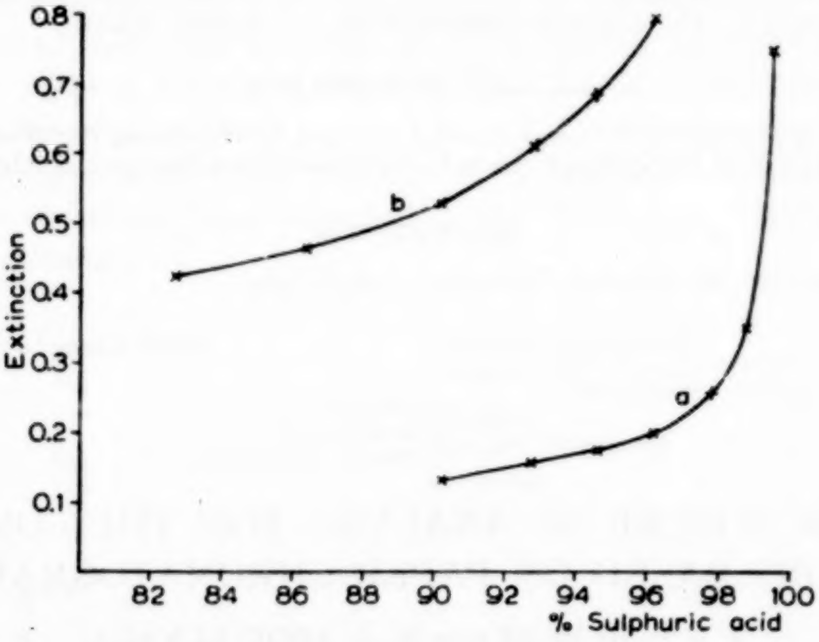

Fig. 1. Extinctions of two series of sulphuric acids containing 20 (Curve a) and 80 (Curve b) mg of 1,1′-dianthrimide standard solution per 100 ml. Wavelength 650 mμ.

From Fig. 1 it is seen that the extinction increased slowly and nearly linearly with the concentration of acid up to about 96%. At higher acid concentrations the extinction rose steeply to high values. The extinction of the solutions was measured immediately after preparation and was found to be constant for about one week, except for the 99.45% acid in which the extinction increased slowly with the time of standing.

In the present investigation a standard solution of 1,1′-dianthrimide in 96.12% sulphuric acid was used, 2 or 8 ml of this solution (corresponding to 20 or 80 mg of reagent) being pipetted into 100-ml volumetric flasks. The flasks were then filled up to volume with sulphuric acids, the strengths of which are given in Fig. 1. For the determination of acids in the range 80 to 96% the addition of 8 ml of standard solution (80 mg of 1,1′-dianthrimide) was found suitable. For acids in the concentration range 96 to about 99.5%, 2 ml of standard solution (20 mg of 1,1′-dianthrimide) were added.

Volumetric flasks with ground glass stoppers are recommended. The solutions should not be exposed to the atmosphere for any length of time. To prevent precipitation of 1,1′-dianthrimide by dilution with water, cells, pipettes etc., should first be cleaned with concentrated sulphuric acid and then with distilled water.

ACKNOWLEDGEMENT

The authors are indebted to Professor HAAKON HARALDSEN for his interest in this investigation and for the facilities placed at their disposal.

SUMMARY

The strength of sulphuric acids in the concentration range 80 to 99.5% can be determined spectrophotometrically at 650 mμ with 1,1′-dianthrimide. 1,1′-Dianthrimide dissolved in concentrated sulphuric acid seems to exist in two forms, the green form concentration increasing with the strength of acid.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour la détermination de la force d'un acide sulfurique (de 80 à 99.5%). On utilise la dianthrimide-1,1′ comme réactif.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung der Stärke von Schwefelsäure (80–99.5%). Zur Messung gelangt die mit einer bekannten Menge Dianthrimid-1,1′ erzeugte grüne Färbung.

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A NEW SCHEME OF ANALYSIS FOR THE COMMON ANIONS BASED ON PAPER CHROMATOGRAPHY

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A scheme of analysis for the common cations based on paper chromatography has already been described; three solvent mixtures were needed and the technique was called the chromatogram comparison method[1].

A differential spraying method for the location, identification and confirmation of the common anions is now described. The method depends on the use of a single solvent mixture (ethanol–pyridine–ammonia). A general mixed spray of Laurents' acid, ammoniacal silver nitrate and fluorescein is used for the location and tentative confirmation of the anions; these are finally confirmed by specific sprays.

EXPERIMENTAL AND RESULTS

Dissolution of the powder

1. A solution is prepared by boiling about 0.2 g of the sample with 2 ml of distilled water. The solution is cooled and centrifuged to remove any precipitate; the clear supernatant solution is used for analysis.

2. Any insoluble salts present after centrifuging are tested for carbonates by the usual tests. They can then be brought into solution by fusion with "AnalaR" sodium carbonate; the fused mass is powdered and 0.2 g of the powder is boiled with 2 ml of distilled water. The solution is cooled and centrifuged, and only the clear supernatant liquid is chromatographed.

Preparation of the chromatograms

The apparatus consists of a glass trough supported in a glass tank, 50 × 25 × 15 cm, tightly covered with a glass plate. It is placed in an insulated cupboard at room temperature.

The best solvent for the separation of the common anions was found to be a mixture of 60 ml of absolute ethyl alcohol, 20 ml of purified pyridine, 16 ml of distilled water, and 4 ml of concentrated A.R. 0.880 ammonia. This homogeneous solvent gave the best separations and most concentrated spots for almost all anions under consideration (see Fig. 1). Some of the solvent is placed in the trough and some in a petri-dish at the bottom of the glass tank.

Filter paper sheets are cut into 5 × 40 cm strips and the trough height is adjusted so that the paper strips can hang from both sides of the trough with their top edges dipping into the solvent.

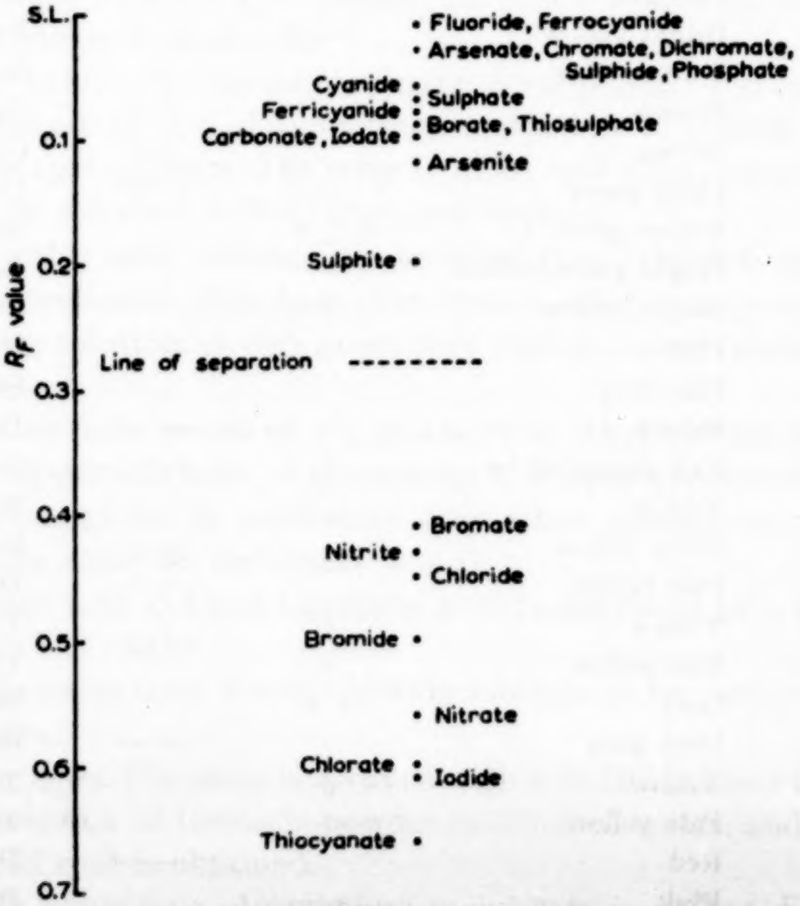

Fig. 1.

For every complete analysis twelve strips should be prepared on one or more tanks with the above solvent mixture. The solvent front should run at least 30 cm from the starting line; this usually takes about 10 hours.

The filter paper sheets must be of proper chromatographic quality. All reagents must be of AnalaR purity.

Analysis of the chromatograms

The strips are removed from the tanks and dried in a stream of hot air. One strip is used for treatment with a freshly prepared general spray consisting of 50 ml of ammoniacal silver nitrate solution, 50 ml of a saturated solution of Laurents' acid in distilled water, and 0.05 g of fluorescein. After spraying the strip is allowed to dry and viewed under U.V. light. In daylight some spots on the strip appear very clearly while others remain pale. The paper strip can be warmed very gently or preferably allowed to stand for one or two hours when the pale spots should appear very clearly in daylight. Table I shows the appearance of anions under U.V. light and in daylight, after treatment with the general spray.

Five strips are used for double spraying while six strips are used for single spraying. This is carried out as follows.

1. A pencilled line is drawn across the strips at an R_F value of 0.28. The upper zone contains fluoride, ferrocyanide, arsenate, chromate, dichromate, sulphide,

TABLE I

Anions	*Appearance in day light*	*Appearance under U.V. light*		
		Bright spots	*Dark spots*	*Colour*
Fluoride	Pale grey		—	Grey
Ferrocyanide	Bright yellow	++		Bright yellow
Arsenate	Green-yellow		—	Green-grey
Chromate	Brown		— —	Dark grey
Dichromate	Brown		—	Green-grey
Sulphide	Dirty green		— —	Dark green-grey
Phosphate	Yellow-green	+++		Bright green-yellow
Cyanide	Bright green-yellow	+++		Bright green-yellow
Sulphate	Bright yellow	+++		Bright yellow
Ferricyanide	Pink		— —	Dark red-violet
Borate	Pale grey		—	Blue
Thiosulphate	Brown		— —	Dark violet-grey
Carbonate	Pale green-yellow	+		Green-yellow
Iodate	Yellow	++		Bright yellow
Arsenite	Dirty yellow		— —	Dark green-grey
Sulphite	Pale brown		— —	Dark grey
Bromate	Yellow	+		Yellow
Nitrite	Pale yellow	+		Yellow
Chloride	Grey	++		Bright yellow
Bromide	Dark grey		— —	Dark grey
Nitrate	Yellow	+		Yellow
Chlorate	Pale yellow	+		Yellow
Iodide	Red		— —	Dark violet
Thiocyanate	Pink	++		Bright yellow

phosphate, cyanide, sulphate, ferricyanide, borate, thiosulphate, carbonate, iodate, arsenite and sulphite. The lower zone contains bromate, nitrite, chloride, bromide, nitrate, chlorate, iodide and thiocyanate.

2. A sheet of aluminium (about 20 × 20 cm) is used to mask one zone while the other is sprayed. During spraying the paper strip is kept taut by fixing "Bulldog" clips to its lower edge.

3. The presence of anions in the upper zone should be confirmed first, while the lower zone is masked. The anions in the lower zone can then be confirmed, after the paper strip has been dried. Double spraying is best carried out in the following order.

Strip 1: Fluoride then chlorate, bromate and nitrate. Strip 2: Arsenate then nitrite. Strip 3: Sulphate then chloride. Strip 4: Cyanide then bromide and thiocyanate. Strip 5: Borate then iodide.

4. Single spraying is carried out for each of the following anions in the upper zone:

Strip 1: Ferrocyanide and ferricyanide. Strip 2: Chromate and dichromate. Strip 3: Arsenite. Strip 4: Iodate. Strip 5: Sulphide, thiosulphate and phosphate. Strip 6: Sulphite and carbonate.

List of confirmatory sprays

Fluoride: R_F value 0.01. 10 ml of 1% zirconium nitrate in water mixed with 10 ml of 0.1% alizarin red S in dilute nitric acid. A bright yellowish-white spot appears against the red-purple back-ground.

Ferrocyanide: R_F value 0.01. 5 g of hydrated ferric chloride in 100 ml of water containing 2 ml of concentrated hydrochloric acid. A prussian blue spot appears[2].

Arsenate: R_F value 0.03. 10% potassium iodide in 2 *N* HCl. A stable dark brown colour appears on gentle warming.

Chromate: R_F value 0.03. 0.2 g of diphenylcarbazide in 100 ml of 2 *N* acetic acid. A deep violet-red colour is obtained.

Dichromate: R_F value 0.03. As for chromate. A deep violet-red colour appears.

Sulphide: R_F value 0.03. 5 g of ammonium molybdate in 100 ml of 2 *N* sulphuric acid. A violet-blue spot appears. The strip is dried and then sprayed with aqueous 5% sodium sulphite solution. A deep blue spot appears.

Phosphate: R_F value 0.03. Ammonium molybdate is prepared as for sulphide. A canary-yellow spot indicates phosphate. The strip is dried and sprayed with aqueous 5% sodium sulphite solution. A dull green spot appears which changes to blue-grey on gentle warming.

Cyanide: R_F value 0.06. 10 ml of 2% guaiacol in ethyl alcohol mixed with 1 ml of aqueous 0.1% copper sulphate. A permanent blue spot appears immediately.

N.B.: This test is given by carbonate only when cyanide is absent from the original solution (R_F value for carbonate = 0.1).

Sulphate: R_F value 0.07. 0.2 g of Laurents' acid in 100 ml of 50% ethanol. A violet spot appears under U.V. light.

Ferricyanide: R_F value 0.08. Ferric chloride solution as for ferrocyanide. A bright green colour appears.

Borate: R_F value 0.09. The strip is sprayed with 2 *N* HCl, allowed to dry, sprayed with a saturated solution of turmeric powder in distilled water, and dried by gentle warming. A pale red spot is obtained.

Thiosulphate: R_F value 0.09. Ammonium molybdate is prepared as for sulphide.

A violet-blue spot appears immediately. The strip is dried and sprayed with aqueous 5% sodium sulphite. A deep blue spot indicates thiosulphate.

Carbonate: R_F value 0.10. 0.1 g of kojic acid and 0.1 g of *o*-coumaric acid dissolved in 100 ml of ethanol. The strip is sprayed, dried, then sprayed with ammoniacal silver nitrate solution and allowed to dry. A dark-brown spot appears in daylight.

N.B.: This test is given by cyanide only when carbonate is absent from the original solution (R_F value for cyanide = 0.06).

Iodate: R_F value 0.10. 1 g of phenylhydrazine hydrochloride in 100 ml of 50% ethanol. A brownish-red spot appears on gentle warming.

Arsenite: R_F value 0.12. Ammoniacal silver nitrate solution. A bright canary-yellow spot appears.

Sulphite: R_F value 0.20. Kojic and *o*-coumaric acids as for carbonate. A medium grey spot appears under U.V. light. The strip is dried and sprayed with ammoniacal silver nitrate solution; a yellowish-white slightly fluorescent spot appears under U.V. light while the strip is still wet. When the strip is dry, a brown spot appears in daylight.

Bromate: R_F value 0.41. 0.02% solution of brucine in 2 N sulphuric acid. A deep red colour appears on gentle warming. When the strip is sprayed with 2 N sodium hydroxide solution, a deep blood-red colour appears immediately.

Nitrite: R_F value 0.43. 0.1 g of *o*-coumaric acid in 100 ml of ethanol. A dark green-grey spot appears under U.V. light.

Chloride: R_F value 0.45. The strip is sprayed with silver nitrate solution and washed immediately in distilled water. It is then dried and sprayed with colourless ammonium sulphide solution. A black spot at the given R_F value indicates chloride[3].

Bromide: R_F value 0.50. 5 g of ferric nitrate in 100 ml of 0.5 N nitric acid. A yellow colour appears on gentle warming.

Nitrate: R_F value 0.56. Brucine in sulphuric acid as for bromate. On gentle warming a red colour appears which changes to yellow. On spraying with 2 N sodium hydroxide solution, an orange-yellow colour develops immediately.

Chlorate: R_F value 0.60. Brucine in sulphuric acid as for bromate. The reddish-brown colour which appears on gentle warming changes to blood-red on spraying with 2 N sodium hydroxide.

Iodide: R_F value 0.61. The strip is sprayed with 5% potassium nitrite solution, dried and sprayed with a starch solution acidified with some drops of sulphuric acid. A deep blue colour appears.

Thiocyanate: R_F value 0.66. Ferric nitrate reagent as for bromide. A blood-red colour appears immediately.

It will be noticed from the above list that the following groups of anions require the same confirmatory spray.

1. Ferrocyanide and ferricyanide. 2. Chromate and dichromate. 3. Sulphide, phosphate and thiosulphate. 4. Carbonate and sulphite. 5. Bromate, nitrate and chlorate. 6. Bromide and thiocyanate.

DISCUSSION

Only 12 drops of test solution are required for the complete analysis of any mixture of the above-mentioned anions. The limit of detection of the method lies between 20 and 100 μg of each anion on the original spot. This corresponds to 0.2–1 g% of each anion in the original solution.

SUMMARY

A paper chromatographic method is described for the qualitative analysis of any mixture of common anions. A single solvent and differential spraying are used.

RÉSUMÉ

Les auteurs ont mis au point un schéma d'analyse qualitative des anions courants, en utilisant la chromatographie sur papier.

ZUSAMMENFASSUNG

Es wird ein qualitativer Analysengang für Anionen mit Hilfe der Papierchromatographie beschrieben.

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DETERMINATION OF METAL IONS IN SOLUTION BY MEANS OF TAA AND EDTA

I. GENERAL INTRODUCTION AND DETERMINATION OF ZINC

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GENERAL INTRODUCTION

In many cases addition of an excess of EDTA to neutral or basic metal salt solutions considerably decreases the metal ion concentration[1]. Addition of calcium chloride to metal–EDTA complex solutions causes a shift of the metal–EDTA equilibrium, resulting in the formation of free metal ions[2].

Thioacetamide (TAA) decomposes slowly in acid and alkaline solutions to form hydrogen sulfide by hydrolysis[3]; this can be applied to the homogeneous precipitation of metal sulfides under well-defined conditions.

The combination of these three phenomena suggests many possibilities for the quantitative determination of metal ions in the hydrogen sulfide separation system. With the aid of TAA and EDTA, however, other subdivisions of the metal ions can be made, some improved separations are possible and precipitates with excellent filtration properties are obtained[4].

Flaschka[2] first described the behaviour of many metal ions in solution with TAA, both in absence and presence of EDTA and calcium ions but he did not mention any quantitative applications.

In Table I and II are summarised the observations made by Flaschka and our-

TABLE I

INFLUENCE OF EDTA AND CALCIUM CHLORIDE ON THE PRECIPITATION OF METAL IONS BY AMMONIA

Metal ion	*NH_4OH*	*EDTA + NH_4OH*	*EDTA + NH_4OH + $CaCl_2$*
Cu	—	—	—
Pb	+	—	—
Cd	—	—	—
Hg	+	—	—
Bi	+	—	—
As(III)	—	—	—
As(V)	—	—	—
Sb(III)	+	+	+
Sb(V)	+	+	+
Sn(II)	+	+	+
Sn(IV)	+	+	+
Zn	—	—	—
Fe(II)	+	—	+
Fe(III)	+	—	+
Co	±	—	—
Ni	—	—	—
Mn	±	—	+
Al	+	—	+
Cr	+	—	±

The symbols in the tables represent:
+ = complete precipitation;
± = incomplete precipitation or precipitation depending on conditions such as concentration, etc.;
— = no precipitation.

selves on the behaviour of solutions containing many metal ions. Table I shows the influence of EDTA and calcium chloride on the precipitation of the metal ions by ammonia. The second column shows the effect of adding ammonia to acid solutions

TABLE II

INFLUENCE OF EDTA AND CALCIUM CHLORIDE ON THE PRECIPITATION OF METAL IONS WITH TAA

Metal ion	*Medium*			
	Acid	*Ammoniacal*		
		TAA	*EDTA + TAA*	*EDTA + TAA + $CaCl_2$*
Cu	+	+	+	+
Pb	±	+	+	+
Cd	±	+	±	+
Hg	+	+	+	+
Bi	+	+	+	+
As(III)	+	—	—	—
As(V)	+	—	—	—
Sb(III)	+	±	±	±
Sb(V)	+	±	±	±
Sn(II)	+	+	+	+
Sn(IV)	±	+	+	+
Zn	—	+	—	+
Fe(II)	—	+	—	+
Fe(III)	—	+	—	+
Co	—	+	—	±
Ni	—	+	—	±
Mn	—	+	—	+
Al	—	+	—	+
Cr	—	+	—	—

of the metal ions, the third the effect when the solution contains an excess of EDTA, and the fourth the effect of adding excess calcium chloride to the ammoniacal metal solutions containing EDTA.

Table II shows the influence of EDTA and calcium chloride on the precipitation of metal ions with TAA in ammoniacal solution. In the second column the behaviour of metal ions with TAA in acid medium is given since it slightly differs from that with hydrogen sulfide. In the other columns the action of TAA on ammoniacal metal ion solutions is described, as well as the influence of EDTA and calcium chloride on this action.

It is obvious that the familiar quantitative separations involving sulfides and hydroxides can be largely extended by introducing EDTA and calcium chloride as masking and demasking agents. In some cases it depends on the experimental conditions whether an element remains in solution or is precipitated as sulfide or hydroxide. This also increases the number of possible separations.

For quantitative determination, a metal ion need be separated only from those accompanying metals which interfere with the analytical method chosen. The selection of a suitable method of determination is therefore of the greatest importance. In some subsequent papers we will describe determinations of a few metal ions by means of these new possibilities, and show that rapid and simple determinations of small amounts of metals can be carried out with fair accuracy.

I. Determination of Zinc

INTRODUCTION

There is no good specific quantitative method for the determination of zinc in presence of group II and group III elements, hence zinc must be separated from these elements before its determination.

Sulfide separations of the elements of the second group from zinc by means of hydrogen sulfide are generally unsatisfactory; in strongly acid solutions precipitation of cadmium, lead and tin is incomplete, while in solutions of low acidity zinc is coprecipitated[5].

As has been pointed out above, the precipitates obtained with TAA are coarser than those obtained with hydrogen sulfide, relatively free from adhesion to glass walls, and are therefore more suitable for rapid quantitative filtration. Our experiments have shown that zinc can be separated from the group II elements much better by means of TAA than with hydrogen sulfide.

The difficult separation of zinc from the group III elements is also important. Hydroxide separations are usually incomplete. Zinc is normally precipitated at pH 2–3, but this has many disadvantages. The conditions must be carefully controlled and reprecipitation is necessary[5]. According to Tables I and II it should be possible to separate zinc from the other group III elements in two steps: first, zinc is separated from aluminium, manganese and iron by precipitation of the latter elements as hydroxides on addition of calcium chloride to an ammoniacal solution containing EDTA; secondly, zinc is precipitated in the filtrate as sulfide with TAA, while chromium remains in solution. As regards nickel and cobalt, the former can be kept in solution but cobalt is always coprecipitated with zinc.

After the precipitate of zinc sulfide has been dissolved, zinc can be determined by complexometric titration with EDTA, as described by SCHWARZENBACH[6].

In this paper the results of investigations on the determination of zinc in the presence of group III and group II elements are described.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade.

TAA, Merck, 2% and 6% solution in water; hydrochloric acid, 4 *N*; buffer solution, pH = 11 ($NH_4OH - NH_4Cl$); EDTA solution, 0.1 *M* and 0.25 *M*; $CaCl_2$ solution, 0.3 *M* and 0.75 *M*; NH_4Cl solution, 2%, slightly ammoniacal; NH_4Cl solution, 4 *M*; KOH solution, 20%.

Procedure

The determinations are carried out in 15-ml centrifuge tubes. To 5 ml of a slightly acid solution containing 0.6 – 6 mg of zinc, add 1 ml of hydrochloric acid and 1 ml of 2% TAA (or 1 ml of 6% TAA, when the solution contains a high concentration of group II elements). Heat for 20 min in a water bath at 90°. Centrifuge and separate the supernatant liquid from the precipitate by suction through a G4 glass filter stick into another centrifuge tube (see Fig. 1). Wash the precipitate three times with 1 ml of water and transfer the wash water into the second centrifuge tube in the same way. Reduce the volume of the filtrate to 5 ml and decompose the excess of TAA in a water bath at 95°.

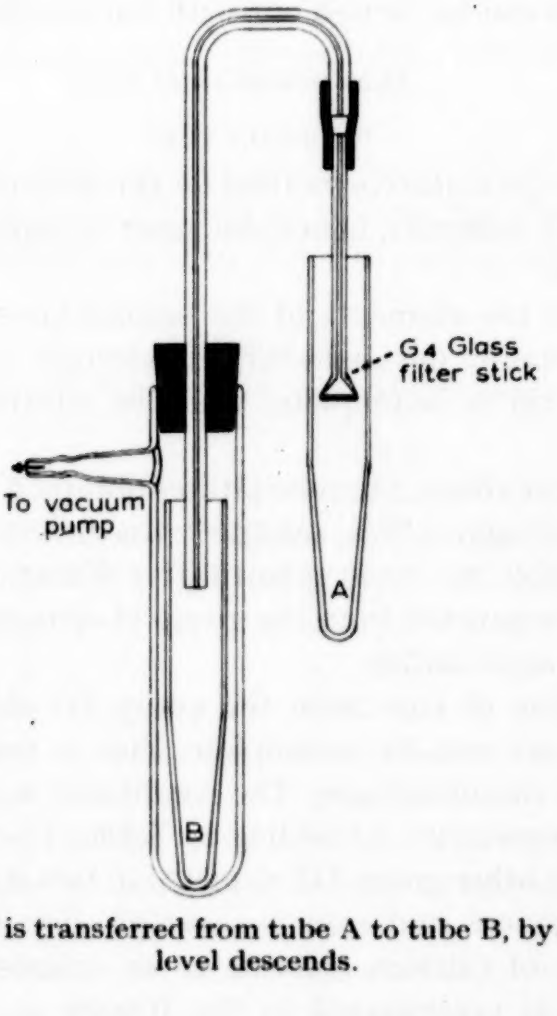

Fig. 1. The supernatant liquid is transferred from tube A to tube B, by raising tube A as the liquid level descends.

Neutralise the solution with KOH (if a permanent precipitate is formed, add a drop of HCl) and add 1 ml of 0.1 *M* EDTA (1 ml of 0.25 *M* if the solution is very concentrated), 1 ml of buffer and 1 ml of 0.3 *M* $CaCl_2$ (1 ml of 0.75 *M* when 0.25 *M* EDTA is used). Heat for 30 min in a water bath at 95°. Centrifuge and separate the precipitate by decanting the liquid into another centrifuge tube. Wash the precipitate three times with a slightly ammoniacal solution of NH_4Cl and decant the wash liquid in the same way. Reduce the volume of the decanted solution to 5 ml by evaporation in a water bath at 95°.

Cool the solution and add 0.5 ml of buffer solution and 1 ml of 2% TAA. Allow to stand for 30 min and then heat for 30 min in a water bath at 80°. Centrifuge and remove the supernatant liquid by suction through a G4 glass filter stick. Take care to remove as little as possible of the precipitate from the tube into the glass filter. Wash the precipitate three times with 1 ml of slightly ammoniacal NH_4Cl solution and remove the wash liquid in the same way.

Dissolve the precipitate in the centrifuge tube and on the filter stick in a few drops of hydrochloric acid. Transfer the combined solutions to a titration beaker, boil to drive out hydrogen sulfide and titrate with EDTA according to the procedure given after the notes.

Notes

1. The procedure outlined above is suitable if Sn, Pb, Cd, Fe(II), Cr, Ni and Co are absent. It can be modified to deal with the presence of most of these elements.

a. The presence of tin should be avoided completely. If tin is present it precipitates as the hydrated oxide, together with iron, aluminium and manganese. This precipitate is very voluminous and coprecipitation of zinc always occurs. In the case of alloys tin does not interfere with the normal course of an analysis, since it is precipitated as $SnO_2 \cdot nH_2O$ during dissolution of the alloy in nitric acid.

b. In strongly acid solutions lead is incompletely precipitated by TAA. It can be separated from zinc as $PbSO_4$ before the zinc is precipitated and determined. It is also possible to precipitate zinc according to the above procedure, and to separate any lead accompanying the zinc as the sulfate.

c. The separation of zinc and cadmium has always been very difficult. In the above procedure, cadmium does not precipitate completely with the group II elements, and there is practically no coprecipitation of zinc with these elements. The residual cadmium precipitates with zinc and it is then possible to separate them completely. After the precipitate has been dissolved, the solution is made 0.3 *N* with respect to hydrochloric acid and 1 ml of 2% TAA is added. After heating for at least 20 and at most 30 min in a waterbath at 80°, there is no precipitation of zinc whilst the precipitation of cadmium is complete, except when there is much cadmium and little zinc; in this case reprecipitation should be carried out.

d. If Fe(II) is present, a few drops of bromine water are added to oxidise all the Fe(II) to Fe(III), before the solution is neutralized.

e. If chromium is present, the solution is heated for 15 minutes, directly after the neutralisation and the addition of EDTA and before the addition of buffer and of calcium chloride. Chromium gives a very stable complex on heating with EDTA and remains completely in solution when this procedure is followed.

f. If nickel is present, it can be separated from zinc, but the amount of zinc present must be known approximately. After separation of the hydroxides, 0.5 ml of buffer, 1 ml of 4 *M* NH_4Cl and not more than twice the required amount of TAA are added to the solution. Only zinc is precipitated and it can be separated before nickel precipitates.

g. If cobalt is present, it always precipitates with zinc and the two metals cannot be separated by the above procedure. Before the titration potassium cyanide is added to mask both cobalt and nickel. Addition of formaldehyde demasks zinc only, which can then be titrated[7].

2. The separation of zinc and aluminium is not complete. A small amount of aluminium remains in the solution; this can be masked by means of ammonium fluoride.

The titration

Reagents: EDTA solution, 0.001 *M* and 0.01 *M*; NaOH solution, 2 *N*; buffer, NH_4OH – NH_4Cl, pH = 10 (7 g of NH_4Cl and 57 ml of concentrated ammonia, diluted to 100 ml); Erio T, 100 mg ground with 10 g NaCl; methyl red, 0.1% in alcohol; NH_4F.

Procedure

a. *Titration with 0.001 M EDTA:* Heat the acid solution containing zinc to 40°. Add two drops of methyl red and neutralise with NaOH. To 25 ml of solution add 0.2 ml of buffer, 750 mg of NH_4F and some Erio T. Titrate till the colour changes from red to pure green;

b. *Titration with 0.01 M EDTA:* The same procedure can be used, but the solution need not be heated. To 25 ml solution 0.5 ml of buffer is added.

Notes

1. Some calcium is always present. Calcium and magnesium can be masked during the titration by means of ammonium fluoride.

2. When determinations are carried out with 0.001 *M* EDTA parallel determination of a known amount of zinc is recommended. The results of titrations with 0.001 *M* EDTA are slightly influenced by the amount of buffer and fluoride added. The amounts given above lead to the best results.

RESULTS

Typical results of the determination of zinc in presence of other elements are shown in Table III.

TABLE III

DETERMINATION OF ZINC IN PRESENCE OF GROUP II AND GROUP III ELEMENTS

Amounts of other elements in mg												*mg Zn present*	*mg Zn found*	*Error in %*
Cu	*Hg*	*Pb*	*Cd*	*As*	*Sb*	*Bi*	*Fe*	*Al*	*Mn*	*Cr*	*Ni*			
6	5	5	3	4	6	3						6.00	5.97	—0.5
0.6	0.5	1	0.6	0.4	0.6	0.7						0.600	0.602	+0.3
3	5			4	6	7						0.600	0.597	—0.5
6	5	10	3	4	6	7						0.600	0.591	—1.5
							3	1	2	3	2	6.00	5.98	—0.3
							3	1		3		6.00	5.97	—0.5
							6	3	6			6.00	6.01	+0.2
							0.6	0.3	0.5	0.6	0.5	0.600	0.606	+1.0
							3	1		3		0.600	0.595	—0.8
							3	1	2	3	2	0.600	0.588	—2.0

The procedure has also been applied to the analysis of an alloy of the National Bureau of Standards (164), containing 21.89% Zn, about 64% Cu, 6% Al, 5% Mn, 2.5% Fe, 1% Sn and traces of Pb, Ni and Si. The mean of 6 determinations was found to be 21.79% with a standard deviation of the mean of 0.02%. The small systematic error is probably due to a coprecipitation of traces of zinc with $SnO_2 \cdot nH_2O$ on dissolving the alloy in nitric acid.

DISCUSSION

The method described above gives correct results for small amounts of zinc in presence of large amounts of other elements present; the experimental technique and equipment are very simple.

The time required for the determination of zinc largely depends on the presence of other elements. Some of them require time-consuming separations (Cd and Pb), while in other cases rapid determinations are possible (Ni and Cr). In general, the time required for the analysis of zinc in mixed samples varies from one to three hours.

ACKNOWLEDGEMENT

The authors are indebted to Prof. Dr. W. van Tongeren for his interest in this investigation and for many suggestions for the improvement of the manuscript.

SUMMARY

The behaviour of metal ions with EDTA and TAA in acid and alkaline solutions is discussed and a specific quantitative determination of zinc is described. The use of TAA instead of hydrogen sulfide provides a much better separation of zinc from the elements of group II. After addition of EDTA and ammonia, iron, aluminium and manganese are precipitated in the filtrate as hydroxides by addition of calcium chloride. Zinc is then precipitated as the sulfide with TAA, while nickel and chromium remain in solution. After the precipitate has been dissolved zinc is determined by chelatometric titration with EDTA. As little as 0.6 mg of zinc can be determined in presence of a large excess of other group II and group III elements.

RÉSUMÉ

Après une introduction générale sur le comportement des métaux en présence d'EDTA et de thioacétamide, les auteurs proposent un dosage spécifique du zinc. Après séparation des autres cations, le zinc est précipité comme sulfure et finalement titré par complexométrie au moyen de l'acide éthylènediaminotétracétique.

ZUSAMMENFASSUNG

Es wird über das Verhalten von Metall-Ionen in Gegenwart von EDTA und Thioacetamid berichtet und eine Bestimmung von Zink beschrieben. Nach Trennung von anderen Kationen wird das Zink als Sulfid gefällt und komplexometrisch mit EDTA bestimmt.

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THE MICRO-HETEROMETRIC DETERMINATION OF PLATINUM, PALLADIUM AND GOLD WITH PAPAVERINE

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INTRODUCTION

In two previous reports on the reactions of the noble metal halides with phenanthroline[1], many final compounds (↓↓) of different composition were stoichiometrically and quantitatively obtained. In addition to this, many series of intermediate compounds (↓) were derived from the curves. Structural formulae for many of the compounds were also suggested. Many methods were given for the determination of platinum, palladium and gold in mixtures and for the determination of phenanthroline. With the exception of palladium, the sensitivities of these reactions were low.

It was suspected that the low sensitivities of the reactions were caused by the presence of two nitrogen atoms in the phenanthrene molecule. We were therefore interested to study heterometrically on a parallel basis the reaction of the noble metal chlorides with *papaverine*, which has only one pyridinic nitrogen atom in the complex molecule. We were surprised to establish that the reactions with the noble metals were 3–4 times as sensitive as when using phenanthroline.

On the other hand, with the exception of platinum iodide, in all reactions with the three metals only *one final* compound, ($MePv_2$↓↓) was always obtained; platinum iodide gave the compound $PtPv_4$↓↓. Nevertheless, the metal-halogeno-papaverine compounds obtained showed many specific properties, depending on the specific halogen used. This enabled us to determine the metals in a single titration. The errors in the determination of the final end-points fluctuated in most cases between zero and one per cent. A titration took 15–20 min, just as with phenanthroline. The longer titration time indicated that the papaverine had to be co-ordinated into the halogeno-complexes of the metals analysed.

The action of papaverine as a pure cation is less probable, for such a reaction would require less titration time. Moreover, we obtained the same molar ratio of [Me] : 2[Pv] with gold chloride as with the other metals, and in the case of platinum iodide we always found the final compound at a molar ratio of 1[Pt] : 4[Pv]. In spite of this, it is very reasonable to suppose that the sequences of *intermediate* compounds possess structures with a salt nature in which the papaverine is complexed with the cation only, while either the halide anion or the metal halogen anion acts as an anion of the salt complex obtained. It is therefore risky to present specific structures for the $MePv_2$↓↓, obtained under the different working conditions.

The differences in the behaviour of the apparently analogously composed final compounds ($MePv_2$↓↓) may be explained partly by differences in the structures and partly by the different solubilities of the various halogeno-compounds obtained.

In this report, parallel experiments were carried out in chloride, bromide, iodide and thiocyanate solutions at pH values of *ca.* 1 and *ca.* 7. The most interesting and successful results were obtained in the thiocyanate and the iodide solutions. In special cases iodide was even more sensitive than the thiocyanate.

In order to give an idea of the sensitivity in the presence of the latter anions, we may cite that *ca.* 0.5 mg of gold or platinum was necessary for the determination of these metals in thiocyanate solutions with papaverine. In the case of palladium, *ca.* 0.3 mg of the metal was sufficient. This is about 3–4 times less than in the corresponding titrations with phenanthroline. On the other hand, if gold or platinum was titrated with papaverine in iodide solution, half of the above amounts was quite sufficient for the same analysis. If both gold and platinum were present in the iodide solution, they could both be determined with precision from two critical points of a single titration curve.

EXPERIMENTAL

Reagents

Papaverine hydrochloricum, Roche DAB VI was used. 0.3758 g was dissolved in 100 ml of water to give a 0.01 *M* solution.

Platinum chloride, Johnson, Matthey & Co. ($H_2PtCl_6 \cdot xH_2O$) about 40% Pt. 1 g was dissolved in 250 ml of water (approx. 0.008 *M*).

Palladium chloride, Johnson, Matthey & Co. 1 g was dissolved in 250 ml of 0.2 *N* HCl. (approx. 0.022 *M* $PdCl_2$ in 0.2 *N* HCl).

Gold chloride (brown), B.D.H. Laboratory reagent. 1 g $HAuCl_4 \cdot 3H_2O$ and 25 ml *N* HCl were dissolved in water to give a volume of 250 ml (approx. 0.01 *M* $HAuCl_4$ in 0.1 *N* HCl).

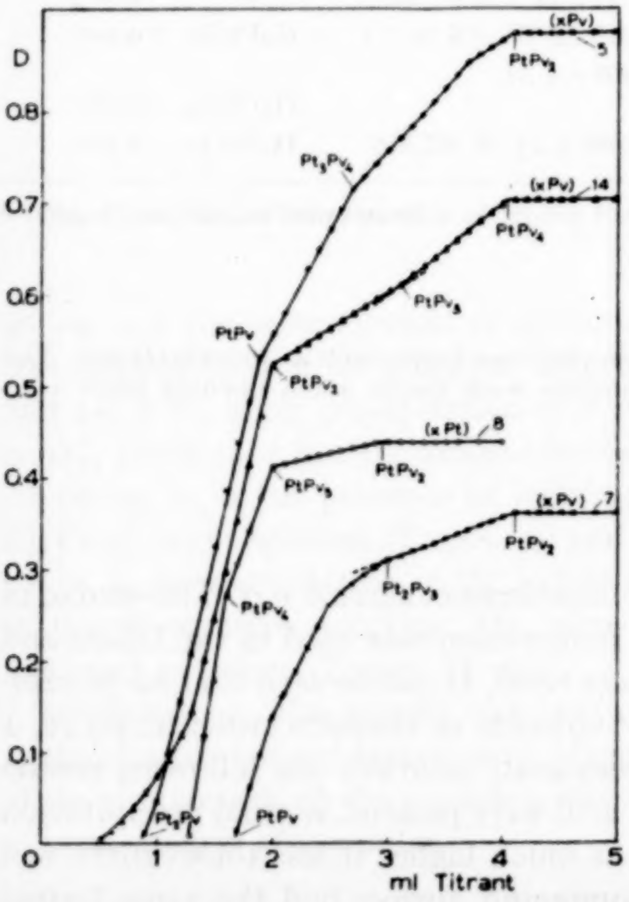


Fig. 1. Titrations of chloroplatinic acid with papaverine and the reverse (Table I).

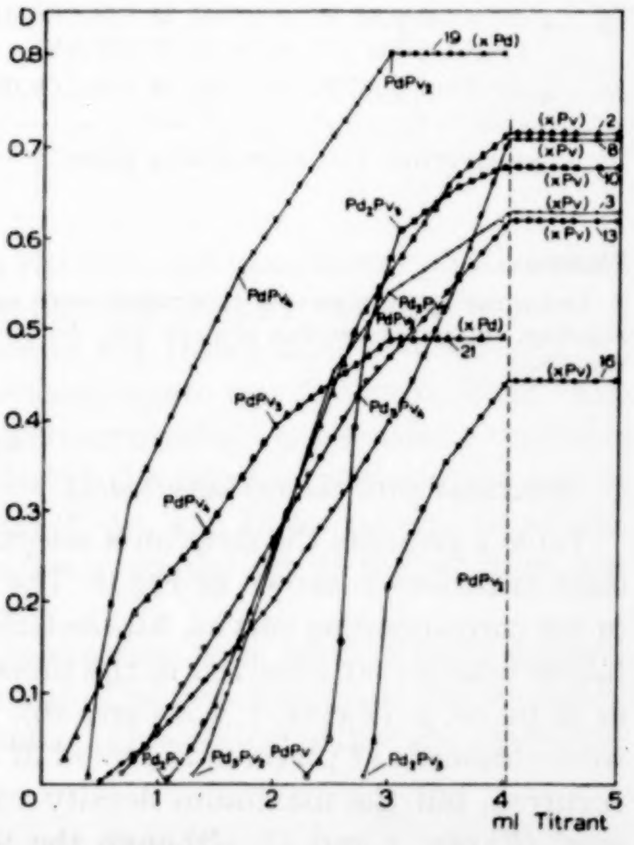


Fig. 2. Titrations of palladium chloride solutions with papaverine and the reverse (Table II).

TABLE I General composition: *a* ml reagents

Expt. No.	*Solution titrated*	*Titrant*		*Titration time in min*
		Name	*Molarity*	
1	6 ml 0.001 M H_2PtCl_6 + 2 ml M HNO_3 + 1 ml M NaCl	Pv	0.003	
2	6 ml 0.001 M H_2PtCl_6 + 2 ml M HNO_3 + 1 ml M KBr	Pv	0.003	
3	3 ml 0.001 M H_2PtCl_6 + 2 ml M HNO_3 + 2 ml 0.25 M KCNS	Pv	0.0015	17
4	3 ml 0.001 M H_2PtCl_6 + 2 ml M HNO_3 + 6 ml 0.25 M KCNS	Pv	0.0015	20
5	3 ml 0.001 M H_2PtCl_6 + 4 ml M HNO_3 + 2 ml 0.25 M KCNS	Pv	0.0015	18
6	3 ml 0.001 M H_2PtCl_6 + 4 ml M HNO_3 + 6 ml 0.25 M KCNS	Pv	0.0015	19
7	3 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COOH + 1 ml 0.1 M CH_3COONa + 2 ml 0.25 M KCNS	Pv	0.0015	25
8	3 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COOH + 1 ml 0.1 M CH_3COONa + 2 ml M KCNS	Pv	0.0015	26
9	3 ml 0.001 M H_2PtCl_6 + 1 ml M CH_3COOH + 1 ml M CH_3COONa + 2 ml M KCNS	Pv	0.0015	
10	3 ml 0.001 M H_2PtCl_6 + 1 ml M CH_3COONa + 3 ml 0.25 M KCNS	Pv	0.0015	
11	4 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COONa + 2 ml M KCNS	Pv	0.002	
12	3 ml 0.001 M H_2PtCl_6 + 3 ml M HNO_3 + 2 ml 0.25 M KCNS + 5 ml alc.	Pv	0.0015	
13	3 ml 0.001 M H_2PtCl_6 + 2 ml M HNO_3 + 1 ml 0.1 M KI	Pv	0.003	7
14	4 ml 0.0005 M H_2PtCl_6 + 2 ml M HNO_3 + 1 ml 0.1 M KI	Pv	0.002	15
15	6 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COONa + 1 ml M NaCl	Pv	0.003	
16	6 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COONa + 1 ml M KBr	Pv	0.003	
17	3 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COONa + 1 ml 0.1 M KI	Pv	0.003	7
18	4 ml 0.0015 M Pv + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	H_2PtCl_6	0.001	18
19	4 ml 0.0015 M Pv + 2 ml M CH_3COOH + 1 ml 0.1 M CH_3COONa + 2 ml 0.25 M KCNS	H_2PtCl_6	0.001	
20	4 ml 0.0015 M Pv + 1 ml M CH_3COONa + 2 ml 0.25 M KCNS	H_2PtCl_6	0.001	

Pv = papaverine; i = intersection point; c = contact point; h = horizontal maximum density line;

Technique

The same apparatus and technique were used as in previous heterometric investigations[2]. The reaction temperature was always 20°. In all experiments with iodide a red Corning filter 2412 was used.

RESULTS

1. *Reactions with chloroplatinic acid*

Table I presents the data on a selection of experiments carried out. The course of some titrations is shown in Fig. 1. The same numeration was used in the tables and in the corresponding curves. All the halides were tried. It can be seen that no precipitation whatsoever occurred in the presence of chloride or bromide either at pH *ca.* 1 or at pH *ca.* 7. (Expts. 1, 2, 15 and 16). In thiocyanate solutions the following results were obtained: at pH *ca.* 1, if 2 ml of M nitric acid were present, normal precipitation occurred, but the maximum density value was much higher if less thiocyanate was used (Expts. 3 and 4), although the final compound always had the same formal composition; but if more nitric acid was used, the influence of the thiocyanate concentration seemed to be annulled (Expts. 5 and 6). In acetic acid solution, at o — *a*) ml H_2O + *x* ml titrant, $T = 20°$

TABLE I

ml titrant used at the		*End-point (↓↓)*			
Init. ppt. point (↑)	*Intermediate intersection points (↓)*	*at ml*	*Maximum density value*	*% error*	*Calculated molar ratios [Pt] : [Pv]*
>5			0.0		
>5			0.0		
0.7	c 2.0 ; 2.9	i 4.10 h	0.86	1.0	1 : 1↓ → 2 : 3↓ → 1 : 2↓↓
1.5	c 2.5 ; 3.0	i 4.10 h	0.41	1.0	4 : 3↑ → ~3 : 4↓ → 2 : 3↓ → 1 : 2↓↓
0.9	1.9 ; 2.7	i 4.10 h	0.88	1.0	2 : 1↑ → 1 : 1↓ → 3 : 4↓ → 1 : 2↓↓
1.1	2.85	i 4.07 h	0.90	0.5	2 : 1↑ → 2 : 3↓ → 1 : 2↓↓
1.8	2.5 ; 3.0	i 4.10 h	0.36	1.0	~1 : 1↑ → 2 : 3↓ → 1 : 2↓↓
2.0		i 4.05 h	0.24	0.0	1 : 1↑ → 1 : 2↓↓
>5			0.0		
>5			0.0		
>5			0.0		
>5			0.0		
0.1	2.0 ; 3.2	i 4.01 h	×1.05	1.0	1 : 2↓ → 1 : 3↓ → 1 : 4↓↓
0.5	1.97; 3.1	i 4.05 h	×0.70	0.0	1 : 2↓ → 1 : 3↓ → 1 : 4↓↓
>5			0.0		
>5			0.0		
>5			×0.02		
1.4	1.6 ; 2.0	i 2.90 h	0.44	2.0	1 : 4↑ → 1 : 3↓ → 1 : 2↓↓
>5			0.0		
>5			0.0		

t = H_2PtCl_6; × = Red filter (Corning 2412).

pH *ca.* 3, if the same amount of platinum was titrated, the maximum optical density was already too low for a normal heterometric titration (Expts. 7 and 8). At pH *ca.* 5 and *ca.* 7 no more precipitation was obtained in the thiocyanate solution (Expts. 9–11); at pH *ca.* 1 in 25% alcohol medium the thiocyanate was dissolved (Expt. 12). At pH *ca.* 1, in the presence of iodide, the heterometrically very sensitive insoluble Pt_1Pv_4↓↓ was obtained (Expts. 13 and 14); but if the titration was carried out at pH *ca.* 7, no precipitation of the iodide occurred (Expt. 17). In the reverse titrations, in the thiocyanate solution, the same dependency on the pH of the solution was observed as before (Expts. 18–20).

Summing up, the results obtained with papaverine were qualitatively entirely analogous to those obtained with phenanthroline. The dependency of the solubility of the compounds on the pH value was also similar. This indicates that the chemistry in both cases is also similar.

2. *Reactions with palladium chloride*

Table II contains the data on a selection of experiments made. Fig. 2 (p. 43) shows

TABLE II General composition: *a* ml reagen

Expt. No.	*Solution titrated*	*Titrant*		*Titration time in min*
		Name	*Molarity*	
1	3 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml M NaCl	Pv	0.0015	
2	3 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 3 ml 0.25 M KCNS	Pv	0.0015	15
3	3 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml M KCNS	Pv	0.0015	12
4	6 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml M NaCl	Pv	0.003	
5	3 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml 0.1 M KBr	Pv	0.0015	
6	3 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml M KBr	Pv	0.0015	
7	3 ml 0.0005 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml 0.1 M KI	Pv	0.0015	
8	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COOH + 1 ml 0.1 M CH_3COONa + 1 ml 0.1 M KCNS	Pv	0.0015	20
9	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COOH + 1 ml 0. 1 M CH_3COONa + 1 ml M KCNS	Pv	0.0015	17
10	6 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml M NaCl	Pv	0.003	14
11	3 ml 0.001 M $PdCl_2$ + 1 ml M CH_3COONa	Pv	0.0015	
12	3 ml 0.001 M $PdCl_2$ + 1 ml M CH_3COONa + 1 ml 0.25 M KCNS	Pv	0.0015	25
13	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml 0.25 M KCNS	Pv	0.0015	18
14	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml M KCNS	Pv	0.0015	15
15	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml 0.1 M KBr	Pv	0.0015	39
16	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml M KBr	Pv	0.0015	38
17	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml 0.1 M KI	Pv	0.003	
18	4 ml 0.0015 M Pv + 1 ml M HNO_3 + 1 ml 0.25 M KCNS	$PdCl_2$	0.001	19
19	4 ml 0.0015 M Pv + 2 ml M CH_3COOH + 1 ml 0.25 M KCNS	$PdCl_2$	0.001	18
20	4 ml 0.0015 M Pv + 1 ml M CH_3COOH + 1 ml M CH_3COONa + 1 ml 0.25 M KCNS	$PdCl_2$	0.001	19
21	4 ml 0.0015 M Pv + 1 ml M CH_3COONa + 1 ml 0.25 M KCNS	$PdCl_2$	0.001	22
22	4 ml 0.0015 M Pv + 5 ml 0.2 M Na_2HPO_4 + 1 ml 0.25 M KCNS	$PdCl_2$	0.001	50

Pd = $PdCl_2$. For other symbols, see Table I.

the courses of a few titrations. At pH *ca.* 1, no precipitation occurred in the chloride or the bromide solutions (Expts. 1, 4, 5 and 6), but at pH *ca.* 7 in both cases precipitation occurred (Expts. 10, 15 and 16), in contrast to the behaviour of phenanthroline. In the presence of iodide the following results were obtained: if the usual amount of palladium was taken, precipitation occurred at pH *ca.* 1 with the first drops of papaverine, but no regular heterometric titration could be carried out. However, if half of this amount of palladium was titrated (Expt. 7), no precipitation at all occurred. At pH *ca.* 7 the titration was just as unsuccessful (Expt. 17). The following results were obtained in the thiocyanate solution: the precipitation was equally successful whether the palladium was titrated with papaverine at pH *ca.* 1 or pH *ca.* 7 (Expts. 2, 3, 8, 9, 12, 13 and 14), but in almost all cases the maximum density values were lower with higher amounts of thiocyanate. In addition, at pH *ca.* 7 higher maximum densities were obtained if less sodium acetate was present (Expts. 12 and 13). In contrast to this, in the reverse titrations the maximum density values decreased with rise in the pH value of the solution (Expts. 19–22). Similar phenomena were observed when phenanthroline was used.

3. *Reactions with gold chloride*

Table III contains the data on a selection of experiments. Fig. 3 (p. 51) shows the course of a few experiments. The reaction of gold with papaverine in the presence of halides

(20 — *a*) ml H_2O + *x* ml titrant, $T = 20°$ TABLE II

ml titrant used at the		*End-point (↓↓)*			*Calculated molar ratios [Pd]:[Pv]*
Init. ppt. point (↑)	*Intermediate intersection points (↓)*	*at ml*	*Maximum density value*	*% error*	
		>5	0.0		
1.2		i 4.05 h	0.72	0.0	2 : 1↑ 1 : 2↓↓
1.4	i 3.0	i 4.04 h	0.63	0.2	~3 : 2↑ → 2 : 3↓ → 1 : 2↓↓
		>5	0.0		
		>5	0.09		
		>5	0.0		
			×0.0		
0.6		i 4.04 h	0.71	0.2	1 : 2↓↓
1.8	i 2.4	i 4.02 h	0.56	0.6	~1 : 1↑ → 1 : 2↓↓
2.4	3.05	3.98	0.68	1.2	~1 : 1↑ → 2 : 3↓↓ → 1 : 2↓↓
		>5	0.0		
0.6		i 4.10 h	0.80	1.0	1 : 2↓↓
0.7	2.7	4.03	0.62	0.4	3 : 4↓ → 1 : 2↓↓
1.3	i 2.5	i 4.04 h	0.44	0.2	3 : 2↑ → ~3 : 4↓ → 1 : 2↓↓
3.0		i 4.00 h	0.43	1.0	2 : 3↑ → 1 : 2↓↓
2.9		i 4.01 h	0.44	0.8	2 : 3↑ → 1 : 2↓↓
		0.2	×0.17		
0.3	c 1.1 ; c ~2.05	i 2.88 h	0.78	2.7	~1 : 6↓ → 1 : 3↓ → 1 : 2↓↓
0.5	0.75; 1.7	i 3.00 h	0.80	1.3	~1 : 4↓? → 1 : 2↓↓
0.4	c 1.3	i 3.00 h	0.66	1.3	~1 : 4↓ → 1 : 2↓↓
0.2	0.8 ; 1.4; 2.0	i 3.00 h	0.49	1.3	1 : 6↓ → 1 : 4↓ → 1 : 3↓ → 1 : 2↓↓
1.0	~1.5	i 2.90 h	0.19	2.0	1 : 6↑ → 1 : 4↓ → 1 : 2↓↓

showed some features not met before: the most sensitive reactions were those with the bromide or with the iodide. No precipitation was obtained with the chloride at pH *ca.* 1 even if the amount of gold was more than usual (Expt. 1). In all other cases, precipitation occurred. At pH *ca.* 1 in the presence of thiocyanate, precipitation occurred only if a higher amount of gold was present (Expts. 2, 3 and 4). The reaction was insensitive to the amount of thiocyanate or nitric acid in solution (Expts. 4 and 5).

At pH *ca.* 7 precipitation occurred in the presence of all the halides including the chloride (Expt. 10). The reaction with the bromide was more sensitive than that with the thiocyanate (Expts. 2, 3, 6 and 7). The reaction was most sensitive with the iodide (Expts. 8, 9 and 14). Probably the sensitivity at pH *ca.* 1 was even higher than at pH *ca.* 7 (Expts. 9 and 14).

GENERAL CONCLUSIONS

In Table IV are summarized all the results of the titrations of single metals with papaverine and vice versa. In each case, the approximate optimum value of the maximum optical density obtained is cited, so that all the results of titrations can be compared. In those experiments when the amount of analysed metal was more or less than usual, this is marked in the table; usual amounts of metal are not marked.

From Table IV, we can come to the following conclusions when a mixture of metal chlorides was analysed.

TABLE III

General composition: *a* ml reagents

Expt. No.	Solution titrated	Titrant		Titration time in min
		Name	Molarity	
1	6 ml 0.001 M $HAuCl_4$ + 2 ml M HNO_3 + 1 ml M NaCl	Pv	0.003	
2	3 ml 0.001 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml 0.25 M KCNS	Pv	0.0015	
3	6 ml 0.001 M $HAuCl_4$ + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	Pv	0.003	20
4	6 ml 0.001 M $HAuCl_4$ + 1 ml M HNO_3 + 6 ml 0.25 M KCNS	Pv	0.003	20
5	6 ml 0.001 M $HAuCl_4$ + 3 ml M HNO_3 + 2 ml 0.25 M KCNS	Pv	0.003	20
6	6 ml 0.001 M $HAuCl_4$ + 2 ml M HNO_3 + 1 ml M KBr	Pv	0.003	17
7	3 ml 0.001 M $HAuCl_4$ + 1 ml M HNO_3 + 4 ml M KBr	Pv	0.002	16
8	4 ml 0.001 M $HAuCl_4$ + 2 ml M HNO_3 + 1 ml 0.1 M KI	Pv	0.002	
9	3 ml 0.0005 M $HAuCl_4$ + 2 ml M HNO_3 + 1 ml 0.1 M KI	Pv	0.00075	16
10	6 ml 0.001 M $HAuCl_4$ + 2 ml M CH_3COONa + 1 ml M NaCl	Pv	0.003	20
11	6 ml 0.001 M $HAuCl_4$ + 2 ml M CH_3COONa + 1 ml 0.25 M KCNS	Pv	0.003	20
12	6 ml 0.001 M $HAuCl_4$ + 2 ml M CH_3COONa + 6 ml 0.25 M KCNS	Pv	0.003	19
13	6 ml 0.001 M $HAuCl_4$ + 2 ml M CH_3COONa + 1 ml M KBr	Pv	0.003	21
14	3 ml 0.0005 M $HAuCl_4$ + 2 ml M CH_3COONa + 1 ml 0.1 M KI	Pv	0.00075	17
15	4 ml 0.003 M Pv + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	$HAuCl_4$	0.002	17
16	4 ml 0.003 M Pv + 1 ml M HNO_3 + 6 ml 0.25 M KCNS	$HAuCl_4$	0.002	19
17	4 ml 0.003 M Pv + 1 ml M CH_3COONa + 2 ml 0.25 M KCNS	$HAuCl_4$	0.002	18

Au = $HAuCl_4$; for other symbols see Table I.

No precipitation of platinum occurred in the chloride solution. Neither palladium nor gold gave a precipitation at pH *ca.* 1; the latter precipitated at pH *ca.* 7, but the results were not very promising.

No precipitation of platinum occurred in the bromide solution. Palladium did not precipitate at pH *ca.* 1, and gave a low density at pH *ca.* 7. Gold in bromide solution gave normal densities at all pH values.

In the presence of thiocyanate, platinum gave the highest density values at pH *ca.* 1, while at pH 5–7 no precipitation occurred. Palladium gave normal results at all pH values. At pH *ca.* 7, the densities were even somewhat higher. Gold gave normal density values only if higher amounts of the metal were present.

In the presence of iodide, platinum gave no precipitation at pH *ca.* 7; high density values were obtained at pH *ca.* 1. Small amounts of palladium gave no precipitation at pH *ca.* 1, and could not be titrated at pH *ca.* 7. High densities were obtained with gold at all pH values.

STRUCTURES

It would be risky to give one kind of structure only. Probably when the titrant is changed and different halides are used, the same empirical compound $MePv_2(\downarrow\downarrow)$ might be constructed differently.

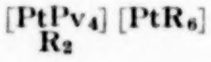
If the sequences of intermediates were considered, the problem of the structure of $MePv_2$ would require an extended report. The first of the writers will discuss this later in connection with other coordinated nitrogen compounds. At the o — *a*) ml H_2O + *x* ml titrant, $T = 20°$

TABLE III

ml titrant used at the		*End-point (↓↓)*			
Init. ppt. point (↑)	*Intermediate intersection points (↓)*	*at ml*	*Maximum density value*	*% error*	*Calculated molar ratios [Au] : [Pv]*
>5			0.0		
>5			0.0		
1.2	c 2.5 ; 3.1	i 4.10 h	0.67	1.0	~2 : 1↑ → 1 : 1↓? → 2 : 3↓ → 1 : 2↓↓
1.4	c 2.9	i 4.08 h	0.62	0.6	~3 : 2↑ → 2 : 3↓ → 1 : 2↓↓
1.2	~3.0	i 4.10 h	0.65	1.0	~2 : 1↑ → 2 : 3↓ → 1 : 2↓↓
0.1	c 1.7 ; 2.9	i 4.00 h	1.05	1.0	~1 : 1↓ → 2 : 3↓ → 1 : 2↓↓
0.4	(?) 1.3 ; 2.0; (?) 2.6	i 3.00 h	0.60	1.0	~1 : 1↓ → 3 : 4↓ → ~2 : 3↓ → 1 : 2↓↓
0.1			× >1.1		
0.1	c 1.2 ; 2.0	i 4.00 h	×0.79	1.0	3 : 2↓ → 1 : 1↓ → 1 : 2↓↓
0.1	i 2.1	i 4.07 h	0.59	0.4	1 : 1↓ → 1 : 2↓↓
1.6	c 2.7	i 4.06 h	0.61	0.2	4 : 1↑ → 3 : 4↓ → 1 : 2↓↓
2.0	i 2.9	i 4.02 h	0.49	0.6	1 : 1↑ → 2 : 3↓ → 1 : 2↓↓
0.1	i 2.2 ; i 3.1	i 4.02 h	0.60	0.6	~1 : 1↓ → 2 : 3↓ → 1 : 2↓↓
0.5	i 2.0 ; i 2.6; 3.17	i 4.00 h	×0.55	1.0	1 : 1↓ → 3 : 4↓ → 2 : 3↓ → 1 : 2↓↓
0.6	c 2.0	i 3.00 h	1.08	1.0	1 : 3↓ → 1 : 2↓↓
0.6	2.25	i 3.00 h	1.13	1.0	~1 : 3↓ → 1 : 2↓↓
0.5		i 3.00 h	0.86	1.0	1 : 2↓↓

present moment, the following structures for the final compounds are suggested.

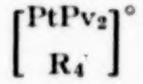
PtPv₂:



$[\underset{R_2}{PtPv_4}]\,[PtR_6]$

(1)

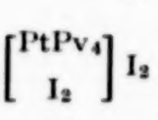
or



$\begin{bmatrix} PtPv_2 \\ R_4 \end{bmatrix}^{\circ}$

(2)

PtPv₄:



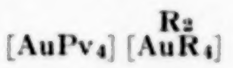
$\begin{bmatrix} PtPv_4 \\ I_2 \end{bmatrix} I_2$

(3)

PdPv₂: $[PdPv_4]\,[PdR_4]$ or $[PdPv_2R_2]^{\circ}$

(4) (5)

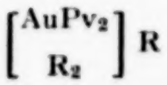
AuPv₂:



$[AuPv_4]\,[\overset{R_2}{AuR_4}]$

(6)

or



$\begin{bmatrix} AuPv_2 \\ R_2 \end{bmatrix} R$

(7)

ANALYTICAL ASPECT

Table V contains a selection of titrations of mixtures of metal chlorides with papaverine at different pH values and in the presence of different anions. Fig. 4 contains the course of a few of these titrations. These experiments were intended to establish the best conditions for the determination of the metals. The critical points of the intermediates obtained are also cited in the table. When a critical point of an inter-

TABLE IV

H_2PtCl_6				$PdCl_2$				$HAuCl_4$			
Titrant	*pH*	R^-	*Approx. maximum density value*	*Titrant*	*pH*	R^-	*Approx. maximum density value*	*Titrant*	*pH*	R^-	*Approx. maximum density value*
Pv	~ 1	Cl^-	> Pt 0.0	Pv	~ 1	Cl^-	> Pd 0.0	Pv	~ 1	Cl^-	> Au 0.0
Pv	~ 7	Cl^-	> Pt 0.0	Pv	~ 7	Cl^-	> Pd 0.7	Pv	~ 7	Cl^-	> Au 0.6
Pv	~ 1	Br^-	> Pt 0.0	Pv	~ 1	Br^-	0.0	Pv	~ 1	Br^-	0.6
Pv	~ 7	Br^-	> Pt 0.0	Pv	~ 7	Br^-	0.4	Pv	~ 7	Br^-	> Au 0.6
Pv	~ 1	CNS^-	0.8	Pv	~ 1	CNS^-	0.6	Pv	~ 1	CNS^-	> Au 0.7
Pv	~ 3	CNS^-	0.4	Pv	~ 3	CNS^-	0.7	Pv	~ 7	CNS^-	> Au 0.6
Pv	~ 5	CNS^-	0.0	Pv	~ 7	CNS^-	0.8	Pv	~ 1	I^-	1.1
Pv	~ 7	CNS^-	0.0	Pv	~ 1	I^-	< Pd 0.0	Pv	~ 7	I^-	< Au 0.6–08
Pv	~ 1	I^-	1.0	Pv	~ 7	I^-	0.2	$HAuCl_4$	~ 1	CNS^-	1.0
				$PdCl_2$	~ 1	CNS^-	0.8	$HAuCl_4$	~ 7	CNS^-	0.9
Pv	~ 7	I^-	0.0	$PdCl_2$	~ 3	CNS^-	0.8				
H_2PtCl_6	~ 1	CNS^-	0.4	$PdCl_2$	~ 5	CNS^-	0.7				
H_2PtCl_6	~ 3	CNS^-	0.0	$PdCl_2$	~ 7	CNS^-	0.5				
H_2PtCl_6	~ 7	CNS^-	0.0	$PdCl_2$	~ 9	CNS^-	0.2				

mediate served as an analytical end-point it is marked in the table as ↓↓. The errors cited in the table concern the first maximum density points.

Before the different methods for the determination of the metals are detailed the results of Table V and the working principles should be discussed.

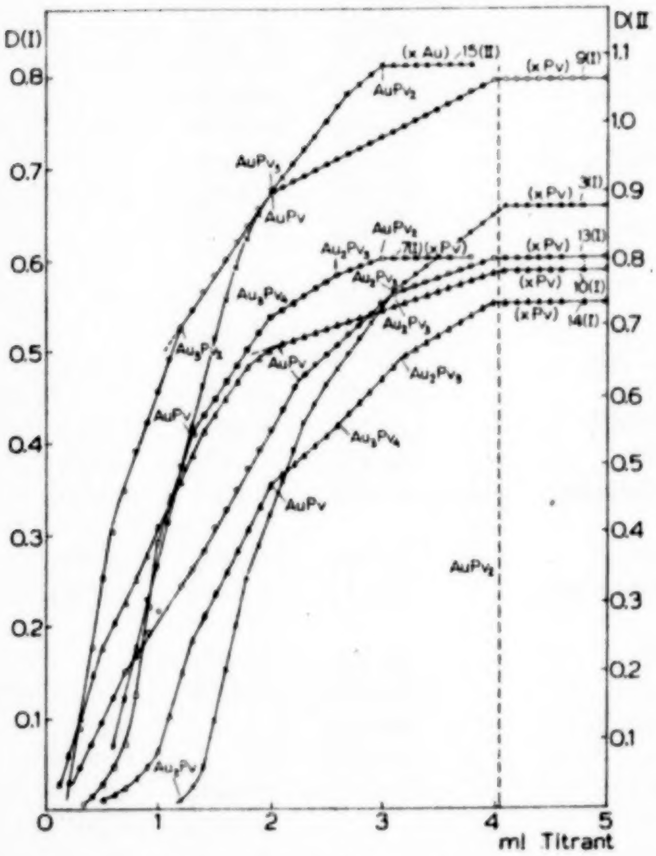


Fig. 3. Titrations of gold chloride solutions with papaverine and the reverse (Table III).

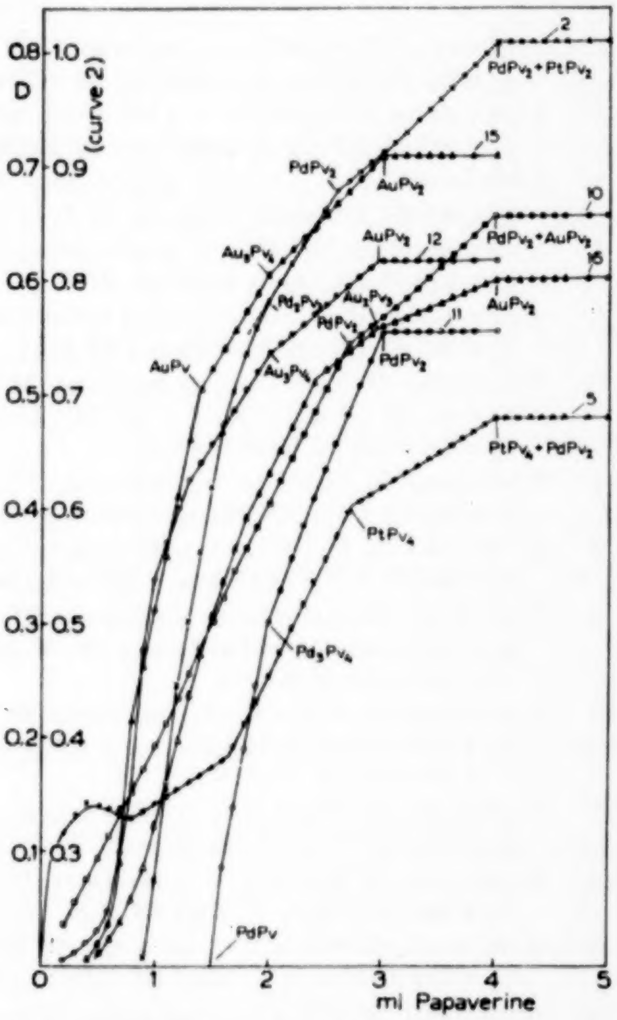


Fig. 4. Titrations of mixtures of platinum, palladium and gold halides with papaverine (Table V).

When mixtures of platinum and palladium were analysed, thiocyanate solution could be used at any pH value: at pH *ca.* 1 (Expts. 1 and 2), *ca.* 5 (Expt. 6) or *ca.* 7 (Expts. 7 and 8). In the last case, the platinum remained dissolved, and the palladium only was determined. At pH 1–5 both metals could be determined from one titration curve: the first end-point coincided with the quantitative formation of the last intermediates. This was either $PtPv_2$ (Expts. 1 and 6) or $PdPv_2$ (Expt. 2), depending on which of the two metals was in excess.

The titration of the mixture of metals could also be carried out in solutions of bromide at pH *ca.* 7; the platinum remained dissolved and the palladium only was determined as $PdPv_2$ (Expt. 11). Similar mixtures of these metals, but in a more dilute solution, could be determined at pH *ca.* 1 in a solution of iodide (Expts. 3–5). Both metals were determined in one titration; the platinum precipitated first.

Mixtures of palladium with gold could be determined at pH *ca.* 1 in solutions of iodide (Expts. 17 and 18). If the palladium was in excess, both metals could be deter-

TABLE V

General composition: *a* ml reagents +

Expt. No.	Composition	% / mg metal Pt	Pd	Au	Molarity of Pv
1	4 ml 0.001 M H_2PtCl_2 + 4 ml 0.0005 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	78.5% 0.7809	21.5% 0.2134		0.003
2	4 ml 0.0005 M H_2PtCl_6 + 4 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	47.8% 0.3905	52.2% 0.4268		0.003
3	3 ml 0.0005 M H_2PtCl_6 + 3 ml 0.0005 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml 0.1 M KI	64.7% 0.2928	35.3% 0.1600		0.003
4	4 ml 0.0005 M H_2PtCl_6 + 3 ml 0.0005 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml 0.1 M KI	70.9% 0.3905	29.1% 0.1600		0.003
5	4 ml 0.0005 M H_2PtCl_6 + 4 ml 0.0005 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml 0.1 M KI	64.7% 0.3905	35.3% 0.2134		0.003
6	6 ml 0.001 M H_2PtCl_6 + 3 ml 0.001 M $PdCl_2$ + 1 ml M CH_3COOH + 1 ml M CH_3COONa + 2 ml 0.25 M KCNS	78.5% 1.1714	21.5% 0.3201		0.004
7	6 ml 0.001 M H_2PtCl_6 + 3 ml 0.001 M $PdCl_2$ + 1 ml M CH_3COONa + 1 ml 0.25 M KCNS	78.5% 1.1714	21.5% 0.3201		0.002
8	6 ml 0.001 M H_2PtCl_6 + 3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml 0.25 M KCNS	78.5% 1.1714	21.5% 0.3201		0.002
9	6 ml 0.001 M H_2PtCl_6 + 3 ml 0.001 M $PdCl_2$ + 3 ml 0.001 M $HAuCl_4$ + 2 ml M CH_3COONa + 1 ml 0.25 M KCNS	56.2% 1.1714	15.4% 0.3201	28.4% 0.5916	0.003
10	6 ml 0.001 M H_2PtCl_6 + 4 ml 0.001 M $PdCl_2$ + 4 ml 0.0005 M $HAuCl_4$ + 2 ml M CH_3COONa + 1 ml 0.25 M KCNS	58.8% 1.1714	21.4% 0.4268	19.8% 0.3944	0.003
11	6 ml 0.001 M H_2PtCl_6 + 3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml M KBr	78.5% 1.1714	21.5% 0.3201		0.002
12	6 ml 0.001 M H_2PtCl_6 + 3 ml 0.001 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml M KBr	66.4% 1.1714		33.6% 0.5916	0.002
13	9 ml 0.001 M $PdCl_2$ + 3 ml 0.001 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml M KBr		61.9% 0.9603	38.1% 0.5916	0.002
14	9 ml 0.001 M $PdCl_2$ + 3 ml 0.001 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml M KBr		61.9% 0.9603	38.1% 0.5916	0.0015
15	6 ml 0.001 M H_2PtCl_6 + 9 ml 0.001 M $PdCl_2$ + 3 ml 0.001 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml M KBr	43% 1.1714	35.3% 0.9603	21.7% 0.5916	0.002
16	4 ml 0.001 M H_2PtCl_6 + 4 ml 0.0005 M $HAuCl_4$ + 2 ml M CH_3COONa + 1 ml 0.1 M KI	66.4% 0.7809		33.6% 0.3944	0.001
17	3 ml 0.0005 M $PdCl_2$ + 3 ml 0.0005 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml 0.1 M KI		35.1% 0.1600	64.9% 0.2958	0.0015
18	5 ml 0.0005 M $PdCl_2$ + 3 ml 0.0005 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml 0.1 M KI		47.4% 0.2668	52.6% 0.2958	0.002
19	4 ml 0.00025 M H_2PtCl_6 + 4 ml 0.00025 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml 0.1 M KI	49.7% 0.1952		50.3% 0.1972	0.0015
20	4 ml 0.00025 M H_2PtCl_6 + 3 ml 0.00025 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml 0.1 M KI	56.8% 0.1952		43.2% 0.1479	0.0015
21	3 ml 0.00025 M H_2PtCl_6 + 6 ml 0.00025 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml 0.1 M KI	33.1% 0.1464		66.9% 0.2958	0.0015
22	4 ml 0.0005 M H_2PtCl_6 + 4 ml 0.001 M $HAuCl_4$ + 2 ml 0.25 M KCNS + 1 ml M HNO_3	33.1% 0.3905		66.9% 0.7888	0.003
23	3 ml 0.001 M H_2PtCl_6 + 3 ml 0.001 M $HAuCl_4$ + 2 ml 0.25 M KCNS + 1 ml M HNO_3	49.7% 0.5857		50.3% 0.5916	0.003

For symbols see Table I.

20 — *a*) ml H_2O + *x* ml *bM* papaverine (Pv), *T* = 20° **TABLE V**

Found								
Init. ppt.		*Intermediates*		*End-point*				*Titration time in min*
at l Pv	*compound*	*ml of Pv used*	*Compounds obtained*	*at ml Pv*	*Compounds obtained*	*Optical density value*	*% error*	
0.4		c 1.61(?); i 2.7	$PtPv_2$ ↓↓	i 4.00 h	$PtPv_2$↓↓ + $PdPv_2$↓↓	0.98	0.0	15
0.5		c 2.0 ; 2.6	c Pd_2Pv_3↓ → $PdPv_2$ ↓↓	i 4.00 h	$PdPv_2$↓↓ + $PtPv_2$↓↓	1.01	0.0	14
0.1		2.0	$PtPv_4$ ↓↓	i 3.00 h	$PtPv_4$↓↓ + $PdPv_2$↓↓	×0.49	0.0	12
0.1		2.7	$PtPv_4$ ↓↓	i 3.70 h	$PtPv_4$↓↓ + $PdPv_2$↓↓	×0.49	0.9	20
0.0		1.67 ; 2.7	$PtPv_4$ ↓↓	i 4.00 h	$PtPv_4$↓↓ + $PdPv_2$↓↓	×0.48	0.0	12
0.5		1.53 ; 2.9	$PtPv$ ↓ → $PtPv_2$ ↓↓	i 4.50 h	$PtPv_2$↓↓ + $PdPv_2$↓↓	0.86	0.0	32
0.5		c 2.7		i 3.00 h	$PdPv_2$↓↓	0.57	0.0	18
0.3		2.1	Pd_3Pv_4↓	i 3.03 h	$PdPv_2$↓↓	0.43	1.0	17
0.3		1.52 ; 2.94	Au_2Pv_3↓ → Pd_3Pv_4↓ →	i 4.00 h	$PdPv_2$↓↓ + $AuPv_2$↓↓	0.59	0.0	13
0.2		2.70	$PdPv_2$ ↓↓	i 4.00 h	$PdPv_2$↓↓ + $AuPv_2$↓↓	0.66	0.0	12
1.5	PdPv	2.0	Pd_3Pv_4↓	i 3.01 h	$PdPv_2$↓↓	0.55	0.3	35
0.3		2.0	Au_3Pv_4↓	i 2.97 h	$AuPv_2$↓↓	0.62	1.0	17
0.3		2.1	Au_3Pv_4↓	i 3.00 h	$AuPv_2$↓↓	0.76	0.0	16
0.7		2.0 ; 2.75	$AuPv$ ↓ → ~Au_3Pv_4↓	i 4.00 h	$AuPv_2$↓↓	0.66	0.0	18
0.5		1.4 ; 2.0	$AuPv$ ↓ → Au_3Pv_4↓	i 3.00 h	$AuPv_2$↓↓	0.70	0.0	16
0.5		2.4 (?); 3.0	Au_2Pv_3↓	i 4.00 h	$AuPv_2$↓↓	×0.60	0.0	24
0.1		1.4 ; 2.5	Au_2Pv_3↓ ?	i 4.00 h	$AuPv_2$↓↓ + $PdPv_2$↓↓	×0.31	0.0	14
0.0		2.56	$PdPv_2$ ↓↓	i 4.00 h	$PdPv_2$↓↓ + $AuPv_2$↓↓	×0.30	0.0	13
0.2		2.1 ; 2.7	$PtPv_3$ ↓ → $PtPv_4$ ↓↓	i 4.00 h	$PtPv_4$↓↓ + $AuPv_2$↓↓	×0.83	0.0	15
0.2		1.08 ; 1.9 ; 2.62	Pt_2Pv_3↓ → $PtPv_3$ ↓ → $PtPv_4$ ↓↓	i 3.68 h	$PtPv_4$↓↓ + $AuPv_2$↓↓	×0.65	0.5	15
0.2		1.30 ; 2.05; 3.0	$PtPv_4$ ↓↓ → $AuPv$ ↓	i 4.00 h	$PtPv_4$↓↓ + $AuPv_2$↓↓	×0.92	0.0	15
0.9		c.i. 2.03 ; 2.85		i 4.00 h	$PtPv_2$↓↓ + $AuPv_2$↓↓	0.52	0.0	15
0.5		1.75 ; 2.35; 3.06		i 4.00 h	$PtPv_2$↓↓ + $AuPv_2$↓↓	0.76	0.0	14

mined in one titration (Expt. 18). The maximum density was low; probably more of the metal should have been used.

Mixtures of palladium and gold (Expts. 13 and 14) could also be titrated at pH *ca.* 1 in bromide solution; the palladium remained dissolved, and the gold was determined.

Mixtures of platinum and gold could be titrated at pH *ca.* 1 in bromide solution; the platinum remained dissolved and the gold was determined (Expt. 12). The sum of both metals could be determined at pH *ca.* 1 in thiocyanate solution (Expts. 22 and 23). Only gold was determined at pH *ca.* 7 in the iodide solution (Expt. 16). Both metals could be determined at pH *ca.* 1 in iodide solution in one titration, but the metal solution had to be more dilute (Expts. 19–21). The platinum always precipitated first.

METHODS

General remarks

1. In all the following determinations, the error at the first maximum density point was between zero and one per cent.

2. The intermediate end-point was always obtained from the intersection of the two adjacent lines (branches). The error at this point could be greatly reduced after experience had been gained in the method concerned.

3. In all titrations with iodide a red filter (Corning 2412) should be used.

1. *Determination of platinum*

Method A: Approximately 0.5 mg of platinum (as H_2PtCl_6) in 20 ml of aqueous solution, containing 4 ml of *M* nitric acid and 1–2 ml of 0.5 *M* potassium thiocyanate, was titrated with *ca.* 0.0015 *M* aqueous papaverine. The first maximum density point coincided with the quantitative formation of $PtPv_2\downarrow\downarrow$.

Method B: Approximately 0.4 mg of platinum (as H_2PtCl_6) in 20 ml of aqueous solution, containing 1 ml of 0.1 *M* potassium iodide and 2 ml of *M* nitric acid, was titrated with *ca.* 0.002 *M* aqueous papaverine. The first maximum density point coincided with the quantitative formation of $PtPv_4\downarrow\downarrow$.

2. *Determination of palladium*

Method A: Approximately 0.3 mg of palladium (as chloride) in 20 ml of aqueous solution, containing 1 ml of *M* nitric acid and 1–2 ml of 0.25 *M* potassium thiocyanate, was titrated with *ca.* 0.0015 *M* aqueous papaverine.

Method B: Approximately 0.3 mg of palladium (as chloride) in 20 ml of aqueous solution, containing 1 ml of *M* sodium acetate and 1 ml of 0.25 *M* thiocyanate, was titrated with *ca.* 0.0015 *M* aqueous papaverine

The first maximum density point in both methods A and B coincided with the quantitative formation of $PdPv_2\downarrow\downarrow$.

3. *Determination of gold*

Method A: Approximately 0.5 mg of gold (as chloride) in 20 ml of aqueous solution, containing 2 ml of *M* nitric acid and 1 ml of *M* potassium bromide, was titrated with *ca.* 0.002 *M* aqueous papaverine.

Method B: Approximately 0.3 mg of gold (as chloride) in 20 ml of aqueous solution, containing 2 ml of *M* nitric acid and 1 ml of 0.1 *M* potassium iodie, was titrated with *ca.* 0.00075 *M* aqueous papaverine.

Method C: Approximately 0.3 mg of gold (as chloride) in 20 ml of aqueous solution, containing 2 ml of *M* sodium acetate and 1 ml of 0.1 *M* potassium iodide, was titrated with *ca.* 0.00075 *M* aqueous papaverine.

The first maximum density point coincided with the quantitative formation of $AuPv_2\downarrow\downarrow$ in each of these three methods. Method B was preferable.

4. *Determination of palladium in platinum*

Method A: Proceed as in method 2 B.

Method B: Approximately 1.5 mg of the alloy, or of the metals as chlorides in 20 ml of aqueous solution, containing 2 ml of *M* sodium acetate and *ca.* 1 ml of *M* potassium bromide, was titrated with *ca.* 0.002 *M* aqueous papaverine. The first maximum density point occurred at quantitative formation of $PdPv_2\downarrow\downarrow$. Method A was preferable.

5. *Determination of gold in platinum*

Method A: Approximately 1.5 mg of the alloy or of the metals as chlorides in 20 ml of aqueous solution, was titrated according to method 3 A except that the amount of nitric acid added was reduced to 1 ml.

Method B: Approximately $\geqslant$ 1 mg of the alloy or the metals as chlorides was titrated according to method 3 C but with *ca.* 0.001 *M* aqueous papaverine.

6. *Determination of gold in palladium*

Proceed as in method 5 A but titrate with *ca.* 0.0015 *M* aqueous papaverine.

7. *Determination of gold in platinum and palladium*

$\geqslant$ 2 mg of alloy or metals as chlorides was titrated according to method 5 A.

8. *Determination of platinum and palladium*

Method A: Approximately 1 mg of the alloy or of the metals as chlorides in 20 ml of aqueous solution, containing 1 ml of *M* nitric acid and 2 ml of 0.25 *M* potassium thiocyanate, was titrated with *ca.* 0.003 *M* aqueous papaverine. Two critical points were obtained. The first point (the last intersection point) coincided with the quantitative formation of $PdPv_2$ (↓) or of $PtPv_2$ (↓). (The metal which was in excess precipitated at this point). The second point (the first maximum density point) coincided exactly with the quantitative formation of $PtPv_2\downarrow\downarrow + PdPv_2\downarrow\downarrow$.

Method B: Approximately 0.5 mg of the alloy or of the metals as chlorides in 20 ml of aqueous solution, containing *ca.* 1 ml of *M* nitric acid and 1 ml of 0.1 *M* potassium iodide, was titrated with *ca.* 0.003 *M* aqueous papaverine. Two critical points were obtained. The first point (the last intersection point) coincided with the quantitative formation of $PtPv_4$ (↓). The second point (the first maximum density point) coincided exactly with the quantitative formation of $PtPv_4\downarrow\downarrow + PdPv_2\downarrow\downarrow$.

Method C: Approximately 1.5 mg of the alloy or of the metals as chlorides in 20 ml of aqueous solution, containing 1 ml of *N* acetic acid, 1 ml of *M* sodium acetate and 2 ml of 0.25 *M* potassium thiocyanate was titrated with *ca.* 0.004 *M* aqueous papaverine. Two critical points were obtained. The first point (the last intersection point) coincided with the quantitative formation of $PtPv_2\downarrow\downarrow$. The second point (the first maximum density point) coincided exactly with the quantitative formation of $PtPv_2\downarrow\downarrow + PdPv_2\downarrow\downarrow$.

9. *Determination of palladium and gold (in alloys of platinum, palladium and gold)*

Approximately 2 mg of the alloy or metals as chlorides in 20 ml of aqueous solution, containing 2 ml of *M* sodium acetate and 1 ml of 0.25 *M* potassium thiocyanate were titrated with *ca.* 0.003 *M* aqueous papaverine. Two critical points were obtained; the first point (the last intermediate point) coincided with the quantitative formation of $PdPv_2$ ($\downarrow\downarrow$). The second point (the first maximum density point) coincided exactly with the quantitative formation of $PdPv_2\downarrow\downarrow + AuPv_2\downarrow\downarrow$.

10. *Determination of platinum and gold*

Method A: Approximately 0.4 mg of the alloy or metals as chlorides was titrated according to method 8 B but with *ca.* 0.0015 *M* aqueous papaverine. Two critical points were obtained. The first point (the last intersection point) mostly coincided with the quantitative formation of $PtPv_4(\downarrow\downarrow)$, while the second point coincided exactly with that of $PtPv_4\downarrow\downarrow + AuPv_2\downarrow\downarrow$.

Method B: 1.2–1.5 mg of the alloy or the metals as chlorides was titrated according to method 8 A. The first maximum density point coincided exactly with the quantitative formation of $PtPv_2\downarrow\downarrow + AuPv_2\downarrow\downarrow$.

11. *Determination of papaverine*

Approximately 2 mg of papaverine in 20 ml of aqueous solution, containing 1 ml of *M* nitric acid and 1 ml of 0.25 *M* potassium thiocyanate, were titrated with aqueous *ca.* 0.001 *M* palladium chloride, or gold chloride.

The first maximum density point coincided with the quantitative formation of $MePv_2\downarrow\downarrow$.

SUMMARY

The reactions between papaverine and platinum(IV), palladium(II) or gold(III) in chloride, bromide, iodide and thiocyanate solutions, were studied heterometrically at pH values 1–9. The sequences and structures of intermediate and final compounds are discussed; the final compounds usually had the composition $MePv_2$. Methods are presented for the determination of the metals (0.3–0.5 mg) singly or in mixtures. In mixtures, all three metals could be determined directly from one or two titration curves.

RÉSUMÉ

Une étude hétérométrique a été effectuée sur les réactions se produisant entre la papavérine et le platine(IV), le palladium(II) et l'or(III) dans des solutions renfermant chlorure, bromure, iodure et thiocyanate. Plusieurs méthodes sont proposées pour le dosage de ces métaux (Pd, Au, Pt).

ZUSAMMENFASSUNG

Der Verlauf der Reaktionen zwischen Papaverin und Platin(IV), Palladium(II) und Gold(III) in Gegenwart von Chlorid, Bromid, Jodid und Thiocyanat wurde heterometrisch untersucht. Methoden zur Bestimmung dieser Metalle werden beschrieben.

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POLAROGRAPHIC DETERMINATION OF MANGANESE

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INTRODUCTION

Although several polarographic methods for the determination of manganese have been devised, none is applicable to every kind of sample. VON STACKELBERG, KLINGER, KOCH AND KRATH[1] neutralized an acidic solution of the sample with barium carbonate to precipitate iron(III) and chromium, and measured the height of the cathode manganese(II) wave in the supernatant solution. Large amounts of nickel (and also of many other elements) or cobalt interfere with the measurement of the manganese diffusion current in this procedure, and necessitate a tedious preliminary separation of manganese as the dioxide. In addition, there would appear to be considerable danger of coprecipitation when traces of manganese are being determined.

VERDIER[2] recommended the use of a cyanide medium for the determination of manganese in the presence of chromium(III), copper, iron(II), and zinc, which were said to be polarographically inert in such a medium, and stated that cobalt was the only common interfering element. However, HUME AND KOLTHOFF[4] have since reported that nickel also yields a wave overlapping the manganese wave[3], and that chromium(III) will also interfere to the extent that it is present as $[Cr(CN)_6]^{-3}$.

VERDIER[5] also discovered an anodic wave corresponding to the oxidation of manganese(II) to manganese(III) in a strongly alkaline tartrate solution, and applied this to the determination of manganese in the presence of iron, nickel, and cobalt. Little information has been available concerning the effects of other elements that might be present.

A much more versatile method, developed by KOLTHOFF AND WATTERS[6], involves the measurement of the height of the cathodic manganese(III) wave in a moderately acidic pyrophosphate solution. Chloride, cerium, chromium, vanadium, and large amounts of iron interfere; although the metals can be removed by precipitation with pyridine, the chemical pretreatment required is rather lengthy. It is also disadvantageous that the manganese(III) complex is reduced at an appreciable rate by metallic mercury.

This paper describes a method employing the alkaline tartrate supporting electrolyte devised by VERDIER[5]. Controlled 1/n potential electrolysis is used to remove interfering elements or render them innocuous, and also to ensure that no error can result from air-oxidation of the powerfully reducing manganese(II) complex prior to the polarographic measurement. The method is simple and accurate and is subject to no known interferences. It should be applicable to the determination of manganese in any kind of sample.

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* Based on a thesis submitted by HENRY A. CATHERINO to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the B.S. in Chemistry degree, 1959.

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EXPERIMENTAL

Polarograms were obtained with a specially-designed recording polarograph which has been described elsewhere[7]. An H-cell[8] provided with a sintered-glass gas-dispersion cylinder for rapid deaeration[9] was used to obtain the data shown in Table I. A silver–silver chloride–saturated potassium chloride reference electrode was employed, but all half-wave potentials have been recalculated to refer to the more customary saturated calomel electrode. Frequent replacement of the agar bridge was necessary, apparently because of the fairly rapid diffusion of complex chloroargentous ions from the reference electrode compartment into the bridge, so that the agar deteriorated rapidly. Silver–silver chloride reference electrodes do not appear to be suitable for routine use with this type of cell.

Controlled-potential electrolyses were carried out with an Analytical Instruments, Inc. (Bristol, Conn.) potentiostat and a double-diaphragm cell with a conical working-electrode compartment[10]. Polarograms of the electrolyzed solutions were obtained without removing them from the cell by inserting a dropping electrode through a 10-mm i.d. vertical tube which was sealed to the horizontal cross-member of the cell and which provided access to the solution in the working electrode compartment. The cell was immersed in a water thermostat at 25.00 ± 0.02°. The silver–silver chloride reference electrode described by MEITES AND MOROS[11] was used without difficulty for both the electrolyses and the subsequent polarograms.

Reagent-grade chemicals were employed throughout. Mercury was purified by the procedure of MEITES AND MOROS[11]. Prepurified nitrogen was scrubbed with chromous chloride to ensure complete removal of oxygen.

DATA AND DISCUSSION

Data on the polarographic characteristics of 29 common metal ions in a supporting electrolyte containing 2.0 F sodium hydroxide and 0.25 F sodium tartrate are shown in Table I. The technique used in obtaining these data, and the precautions adopted to ensure their reliability, have been described elsewhere[12]. With a few exceptions which are probably due to the difference in supporting electrolyte compositions, these values are in generally good agreement with those obtained for a few of these ions in 0.1 F sodium hydroxide–0.5 F sodium tartrate by LINGANE[13].

From this information on the polarographic characteristics of manganese(II) and (III) in this medium, it is evident that any manganese(III) formed by air-oxidation during the preparation of the solution could be quantitatively re-reduced to manganese(II) by controlled-potential electrolysis even if the working electrode potential were maintained at a value as positive as —0.8 V *vs.* S.C.E. However, this is so near the foot of the manganese(III) wave that the reduction would proceed only very slowly, and it is therefore advantageous to employ a potential at least as negative

TABLE I

HALF-WAVE POTENTIALS OF METAL IONS IN 2.0 *F* SODIUM HYDROXIDE – 0.25 *F* SODIUM TARTRATE

Element and oxidation state	$E_{\frac{1}{2}}$ *(V) vs. S.C.E.*	*Oxidation state of product*	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ *(mV)*	*Notes*
As(III)	(—0.310)	V	+38	Very w.-d.
As(V)	NR			
Bi(III)	—0.961	0	—81	W.-d.
Cd(II)	—0.856	0	—26	Very w.-d.[a]
Ce(III)	(—0.30)	IV	+91	I.-d.
Ce(IV)	—0.3		—100	All very i.-d.
	—0.7		—100	
	—1.0		—100	
	—1.3	III[b]	—100	
Co(II)	—1.65	0	—80	I.-d.
Cr(III)	NR			
Cr(VI)	—0.913	III[b]	—92	W.-d.
Cu(II)	—0.52	0	—40	W.-d.
Fe(II)	(—1.00)	III	+58	W.-d.
	—1.38	0[c]	—135	I.-d.
Fe(III)	—1.00	II	—58	W.-d.
	—1.38	0[c]	—135	I.-d.
Mn(II)	(—0.46)	III	46	W.-d.
	—1.82	0	—40	I.-d.
Mn(III)[d]	—0.88	II	—80	Fairly i.-d.
	—1.82	0	—40	I.-d.
Mo(VI)	NR			
Ni(II)	NR			
Pb(II)	—0.827	0	—35	Very w.-d.
Sb(III)	(—0.389)	V	+45	W.-d.
	—1.332	0	—55	W.-d.
Sb(V)	NR			
Sn(II)[e]	(—1.01)	IV	+56	W.-d.
	—1.19	0	—62	W.-d.
Sn(IV)	NR			
Te(IV)	—1.39	0	—43	W.-d.
Te(VI)	NR			
Tl(I)[e]	—0.52	0	—59	W.-d.
U(VI)[f]	—0.87	?	—66	W.-d.
V(IV)	(—0.41)	V	+113	I.-d.
V(V)	—1.86	IV(?)	—100	I.-d.
W(VI)	NR			
Zn(II)[e]	—1.521	0	—51	W.-d.

[a] Maximum eliminated by 0.002% Triton X-100. [b] Confirmed by controlled-potential electrolysis. [c] The height of this wave is much less than twice that of the first wave, and prolonged controlled-potential electrolysis on its plateau yields Fe(II) as the only identifiable product. [d] Prepared by controlled-potential electrooxidation of Mn(II) in this medium. [e] With 0.002% Triton X-100. [f] Partial precipitation.

as —1.0 V *vs.* S.C.E. in order to achieve essentially complete reduction within a reasonable length of time. At the same time, there is no danger of reducing manganese to the metallic state unless the working electrode potential becomes more negative than about —1.65 V *vs.* S.C.E. In view of these considerations, a working electrode potential of —1.50 V *vs.* S.C.E. was selected for use in subsequent experiments.

The proportionality between the diffusion current of the anodic wave and the concentration of manganese was examined by the following procedure, in which controlled-potential electrolysis was employed to ensure that the manganese was entirely present in the +2 state prior to the polarographic measurement. Exactly 100 ml of 2.0 *F* sodium hydroxide–0.25 *F* sodium tartrate was pipetted into the working-electrode compartment of a controlled-potential electrolysis cell containing about 25 ml of pure mercury, and was deaerated briefly with a rapid stream of nitrogen. The central and auxiliary-electrode compartments of the cell had previously been filled with the supporting electrolyte solution in accordance with the standard procedure[10], and a few drops of saturated hydrazine dihydrochloride solution had been added to the auxiliary-electrode compartment to prevent anodic attack of the platinum wire used as the auxiliary electrode. A measured volume of a standard manganese(II) solution was then added. This usually resulted in the appearance of a yellow to brown color due to manganese(III) formed by reaction with the oxygen dissolved in the standard solution, but no precipitation was ever observed. The solution was then electrolyzed at a working-electrode potential of —1.50 V *vs.* S.C.E. for 45 min. This sufficed to decrease the electrolysis current, which was indicated by the counting rate of an Analytical Instruments, Inc., current integrator connected in series with the cell, to a value indistinguishable from the background current obtained when the supporting electrolyte alone was electrolyzed under the same conditions. In routine work it would, of course, suffice to electrolyze only until about 99.5% of the manganese had been reduced to the +2 state, which would require considerably less time than was used here, and a further saving of time could be achieved by using a smaller volume of solution.

When the electrolysis was complete, the potentiostat was turned off, the nitrogen stream was diverted over the surface of the solution, a dropping electrode was lowered into the solution, and the reference electrode was disconnected from the potentiostat and connected to the polarograph. A typical polarogram of manganese(II) obtained in this way is shown in Fig. 1.

Especially when the concentration of manganese is very small, it is essential to exercise considerable care in the measurement of the diffusion current. This is partly

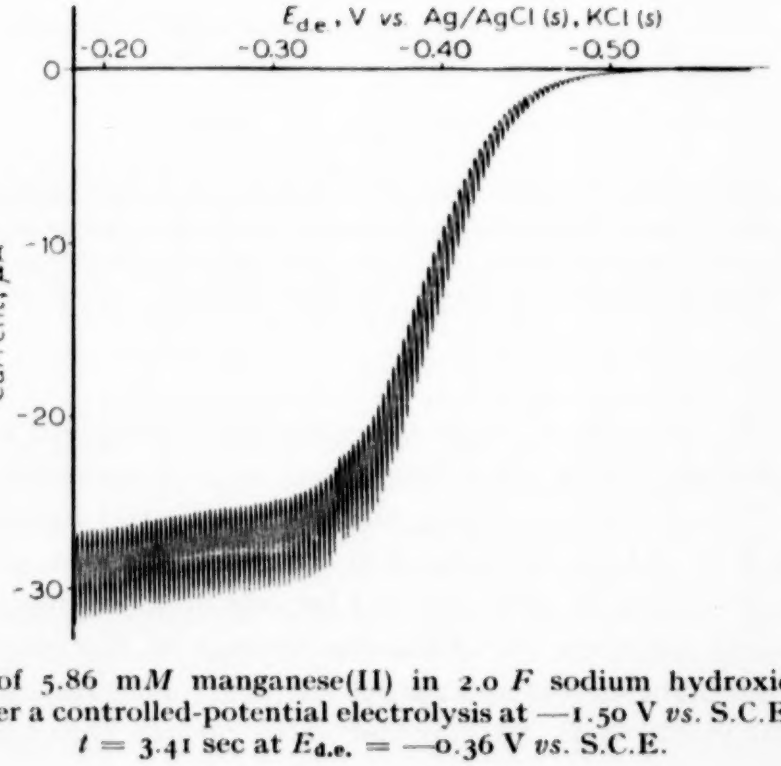

Fig. 1. Polarogram of 5.86 m*M* manganese(II) in 2.0 *F* sodium hydroxide – 0.25 *F* sodium tartrate, obtained after a controlled-potential electrolysis at —1.50 V *vs.* S.C.E. m = 2.93 mg/sec; t = 3.41 sec at $E_{d.e.}$ = —0.36 V *vs.* S.C.E.

due to the fact that the residual current curve is appreciably curved over the range of potentials corresponding to the plateau of the wave, so that the customary extrapolation procedures do not yield a sufficiently accurate estimate of the residual current correction. Another problem is due to the presence of traces of iron in the sodium tartrate employed in the supporting electrolyte. Iron is converted to the ferrous state by a controlled-potential electrolysis at —1.50 V *vs.* S.C.E. in this medium. As shown by the very negative half-wave potential of its anodic wave (—1.00 V *vs.* S.C.E.), ferrous iron is an extremely powerful reducing agent under these conditions, and it reacts rapidly with any traces of oxygen entering from the atmosphere. Hence the anodic diffusion current of ferrous iron decreases slowly on standing, and this, of course, causes the residual current at potentials on the manganese(II) wave to drift toward more positive values. The average magnitude of this effect was found to be about $5 \cdot 10^{-5}$ μA/min. It is thus negligible unless the concentration of manganese is very small. However, it is obviously desirable to record the polarogram as rapidly as possible after the completion of the electrolysis to minimize errors resulting from this cause.

The diffusion currents listed in Table II were obtained by the following procedure. The residual current portion of the polarogram, which begins at about —0.57 V *vs.* S.C.E., was extrapolated linearly toward less negative potentials, and the wave height was taken as the vertical distance between this extrapolated line and the midpoint of the oscillations on the plateau at the arbitrarily selected potential of —0.36 V *vs.* S.C.E., which is just barely on the plateau of the wave. This procedure tends to eliminate errors resulting from the slow air-oxidation of ferrous iron, which merely shifts the entire polarogram upward along the current axis, and is therefore preferable to a correction based on the measurement of the residual current in a separate experiment with the supporting electrolyte alone. Moreover, the use of as positive a potential as possible tends to minimize the effect of the curvature of the residual current curve.

The data shown in Table II demonstrate that the diffusion current thus measured is proportional to the concentration of manganese over at least a 100-fold range with

TABLE II

DIFFUSION CURRENT CONSTANT OF MANGANESE(II) IN 2.0 *F* SODIUM HYDROXIDE – 0.25 *F* SODIUM TARTRATE

c *mmoles/l*	i_d *μA*	i_d/c *μA/mmoles/l*
0.06225	—0.0893	-1.44_{6}
0.2042	-0.294_{3}	-1.43_{6}
0.4009	-0.576_{2}	-1.43_{7}
0.5900	-0.861_{2}	-1.45_{1}
0.7721	—1.137	-1.47_{2}
2.192	—3.162	-1.44_{2}
3.978	—5.68	-1.42_{7}
5.952	—8.58	-1.44_{1}
7.663	—10.92	-1.42_{5}
		Mean: $-1.44_{2} + 0.01_{0}$
		$i_d/cm^{2/3}t^{1/6} = -0.95_{4} \pm 0.00_{7}$

The data were obtained with a capillary for which $m = 1.190$ mg/sec and $t = 5.93$ sec at $E_{d.e.} =$ —0.36 V *vs.*S.C.E.

a mean error of only ±0.7%. The mean value of the diffusion current constant is in good agreement with that (—1.03) obtained by MEITES[14].

It was found that the diffusion current of manganese(II) in this medium is unusually sensitive to changes in supporting electrolyte concentration. In 1.75 *F* sodium hydroxide–0.22 *F* sodium tartrate, for example, the diffusion current is about 20% higher than in 2.0 *F* sodium hydroxide–0.25 *F* sodium tartrate under otherwise exactly the same conditions. The supporting electrolyte concentration must therefore be controlled to within about ±5%; variations equal to or smaller than this have no detectable effect on the diffusion current.

Care in cleaning the cell between analyses is essential to the success of this procedure. If it is merely washed with water, manganese compounds precipitate on its walls and in the pores of the sintered-glass disc and gas-dispersion cylinder, and remain there to contaminate the next sample. This is best eliminated by thorough washing with saturated oxalic acid or with dilute hydrochloric acid containing a little hydrogen peroxide.

The effects of other elements on the measurement of the anodic diffusion current of manganese(II) in this medium can easily be deduced from the data given in Table I. Arsenic(III), antimony(III), tin(II), and vanadium(IV) give rise to waves overlapping the manganese wave, and would therefore interfere seriously.

However, these potential interferences are easily eliminated by the simple expedient of employing an oxidizing attack in the preparation of the sample, because the higher oxidation state of each is polarographically inert in this supporting electrolyte. This inertness is shared by molybdenum, nickel, and tungsten.

When the solution of the sample is electrolyzed at —1.50 V *vs.* S.C.E. to ensure that the manganese is entirely present in the +2 state, a number of other elements will be reduced to the metallic state and removed from the solution. These include bismuth, cadmium, copper, lead, tellurium, and thallium. Cobalt and zinc can also be completely deposited, but only by a very prolonged electrolysis. However, both can be rapidly and completely removed by increasing the working electrode potential to about —1.65 V *vs.* S.C.E.; this may be useful in determining traces of manganese in the presence of a large amount of either of these elements, because it eliminates any effect they may have on the viscosity and tartrate concentration of the solution.

Electrolysis at —1.50 V *vs.* S.C.E. also converts chromium to the +3 state, which is inert, iron to the +2 state, and cerium to the +3 state. Iron(II) gives rise to an anodic wave whose half-wave potential is —1.00 V *vs.* S.C.E. This wave is so well-defined that no further treatment is necessary unless its height is so large as to interfere with the measurement of the height of the manganese wave. However, if the iron/manganese ratio is very large, which will very often be the case, it is necessary to re-oxidize most of the iron to the +3 state by a controlled-potential electrolysis at about —0.8 V *vs.* S.C.E. It suffices to carry out this second electrolysis until the concentration of iron(II) remaining unoxidized becomes roughly equal to the concentration of manganese.

Successive controlled-potential electrolyses at —1.50 V and at —0.8 V *vs.* S.C.E. therefore yield a solution of which cerium(III) is the only constituent that can give rise to a wave interfering with the measurement of the diffusion current of the anodic manganese(II) wave. Unless the cerium/manganese ratio is extremely high, which would be very unusual, the interference of cerium can be eliminated by the following additional steps. A polarogram of the solution is obtained at the end of the electrolysis at —0.8 V *vs.* S.C.E. (or, if the iron/manganese ratio is small enough to permit it, this electrolysis may be omitted and the polarogram may be obtained at the end of the electrolysis at —1.50 V *vs.* S.C.E.), and the diffusion current at —0.36 V *vs.* S.C.E. is obtained as described above. This will include a contribution from the oxidation of cerium(III). If copper is known or believed to be present in the sample, the electrolytic mercury is discarded and replaced by fresh mercury to avoid reoxidation of the previously deposited copper during the next step. This is necessary because copper(II) gives a wave in the range of potentials used to establish the residual current line in measuring the diffusion current in the next step. The potential of the working electrode is now adjusted to —0.44 V *vs.* S.C.E., and the solution is electrolyzed until the electrolysis current becomes constant. Manganese(II) is quantitatively reoxidized to manganese(III) by this electrolysis, but cerium(III) is unaffected. At the completion of this electrolysis a second polarogram is recorded. The diffusion current at —0.36 V *vs.* S.C.E. is measured from this polarogram and subtracted from that obtained from the first polarogram. The difference between these two values is equal to the diffusion current of manganese. By this procedure results accurate to within ±1% were obtained in analyses of samples containing equal concentrations of manganese and cerium.

The considerations just outlined were checked by analyses of synthetic samples containing known amounts of manganese together with various other elements, and were then combined to give the following procedure, which is recommended for use in practical work.

RECOMMENDED PROCEDURE

Weight about 0.5 g of the sample into a small flask and add first 20 ml of 6 *F* perchloric acid, then 10 ml of concentrated nitric acid. Evaporate to fumes of perchloric acid, cool, and transfer to a 100-ml volumetric flask, using 50 ml of 6.5 *F* sodium hydroxide–0.62 *F* sodium tartrate in several small portions for rinsing the flask in which the sample was dissolved. Dilute to the mark with water and mix.

Fill the central compartment of a clean double-diaphragm cell for controlled-potential electrolysis with 2.0 *F* sodium hydroxide–0.25 *F* sodium tartrate and insert the stopper. Into the auxiliary-electrode compartment of the cell pour enough of the same solution so that its level during the electrolysis will be just above that of the solution in the working-electrode compartment, and add a few drops of saturated hydrazine dihydrochloride solution to protect the platinum auxiliary electrode.

Pour about 50 ml of the solution of the sample into the working-electrode compartment, add about 30 ml of pure mercury, and pass a rapid stream of oxygen-free nitrogen into this solution. Adjust a potentiostat to maintain the potential of the working electrode at —1.50 V *vs.* S.C.E., and electrolyse until the current has decreased to a low and practically constant value.

If the percentage of iron in the sample is expected to be greater than about ten times the percentage of manganese, reset the potentiostat to maintain the working electrode potential at —0.8 V *vs.* S.C.E. and electrolyze at that potential until the concentration of iron(II) remaining unoxidized becomes too small to interfere with the measurement of the height of the manganese wave. The time required for this step will depend on the iron/manganese ratio; with optimum stirring in a cell of the type used in these experiments, the time (in minutes) needed can be estimated from the equation $t = 7 \log (\% \text{Fe}/\% \text{Mn})$.

Insert a dropping electrode into the electrolyzed solution, divert the nitrogen stream over the surface of the solution, turn off the potentiostat and the stirrer, and obtain the polarogram of the solution from 0.2 to −0.7 V *vs.* S.C.E. It is convenient to use a low-resistance reference electrode for both the electrolytic and polarographic steps in order to simplify the apparatus required.

Measure the diffusion current at −0.36 V *vs.* S.C.E., employing the modified extrapolation method described above. If cerium is known to be present in the sample, or if the presence of cerium is indicated by a considerable increase of the anodic diffusion current with increasing positive potential on the plateau of the wave, carry out another controlled-potential electrolysis at −0.44 V *vs.* S.C.E. This should be continued until the electrolysis current has become constant. At its conclusion, obtain a second polarogram in the same fashion, and find the diffusion current of manganese as described above.

The concentration of manganese in the prepared solution may be calculated from the equation $C_{\text{Mn}} = -i_d/0.954\, m^{2/3}t^{1/6}$.

Typical results obtained by this method are shown in Table III, in which the polarographic results are seen to agree with the National Bureau of Standards certificate values to well within the probable uncertainties of the latter.

TABLE III

DETERMINATION OF MANGANESE IN NATIONAL BUREAU OF STANDARD SAMPLES

Sample description and N.B.S. designation	*Certified composition*	*% Mn found*
62b	1.29% Mn; 57.4% Cu, 38.0% Zn, 1.0% Al, 1.0% Sn, 0.8% Fe, 0.3% Pb, 0.3% Ni, 0.05% Si, 0.005% As, 0.0005% Sb, 0.004% Ag	1.28_6
72d	0.537% Mn; 1.0% Cr, 0.31% C, 0.28% Si, 0.21% Mo, 0.13% Ni, 0.04% Cu, 0.02% P, 0.01% S, 0.005% V	0.531

SUMMARY

A method for the polarographic determination of manganese is described. It depends on the measurement of the diffusion current of the anodic wave of manganese(II) in a sodium hydroxide–sodium tartrate supporting electrolyte following controlled-potential electrolyses which serve to convert manganese quantitatively into the desired state and to remove other potentially interfering elements or render them innocuous. It is simple, accurate, and specific, and should be applicable to the determination of manganese in any type of sample.

RÉSUMÉ

Une méthode est décrite pour le dosage polarographique du manganèse. Elle est basée sur la mesure du courant de diffusion de la vague anodique du manganèse(II), en utilisant le mélange hydroxyde de sodium, tartrate de sodium comme électrolyte de base.

ZUSAMMENFASSUNG

Beschreibung einer polarographischen Methode zur Bestimmung von Mangan, die auf der Messung des Diffusionstromes der anodischen Welle von Mangan(II) beruht. Als Grundelektrolyt wird eine Mischung von Natriumhydroxyd und Natriumtartrat verwendet.

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SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH 1,4-DIPHENYLTHIOSEMICARBAZIDE WITH SPECIAL REFERENCE TO METEORITES

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For the photometric determination of ruthenium in meteorites, a reagent is needed which will allow 0.5–15 µg Ru to be determined in a 1- or 2-g sample without separation of osmium. 2,4-Diphenylthiosemicarbazide appeared to be a promising possibility. Its use for the determination of 8–30 µg Ru has recently been described[1]. In addition to not reacting appreciably with osmium, it has the advantage of giving a chloroform-extractable ruthenium complex. Adequate sensitivity can thus be obtained by extracting ruthenium into a relatively small volume of chloroform after distillation of the tetroxide, in spite of the mediocre intrinsic sensitivity (0.010 µg Ru/cm^2 for A = 0.001 at 565 mµ).

A trial of 2,4-diphenylthiosemicarbazide for the determination of ruthenium following separation as the tetroxide showed the reagent to have some shortcomings. The color intensity was found to vary somewhat with the concentration of the sulfur dioxide or hydroxylammonium chloride solution in which ruthenium tetroxide is caught on distillation. Stannous chloride is not suitable as an absorbent because it decreases the color intensity. Moreover, the blank absorbance (sulfur dioxide–hydrochloric acid) fluctuates from 0.006 to 0.015 (5 ml chloroform, 1-cm cell).

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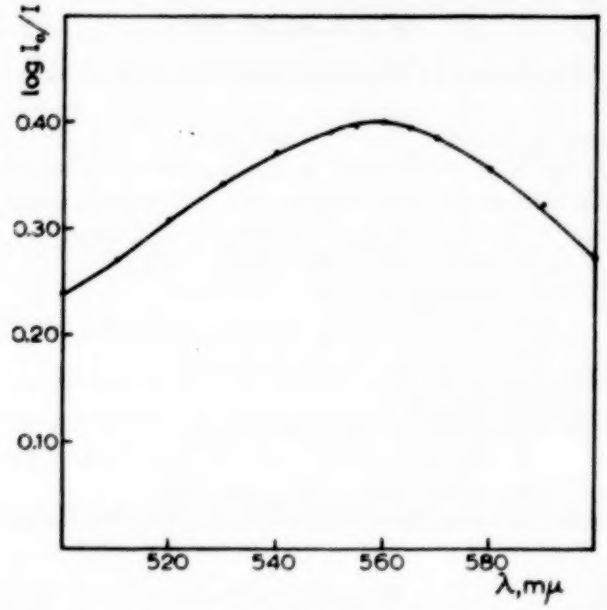

Fig. 1. Absorption curve of ruthenium 1,4-diphenylthiosemicarbazide complex in chloroform (20 μg Ru in 5 ml).

This variability makes 2,4-diphenylcarbazide unsuitable for determining less than 5–10 μg Ru.

We have found that 1,4-diphenylthiosemicarbazide is a more satisfactory reagent. This compound has been listed as a qualitative color reagent for ruthenium but has not been used quantitatively[2]. It gives a blank absorbance of zero under the conditions of the determination. Like the 2,4 isomer, it does not react with osmium and its red-violet ruthenium complex is extractable into chloroform. The sensitivity is 0.010

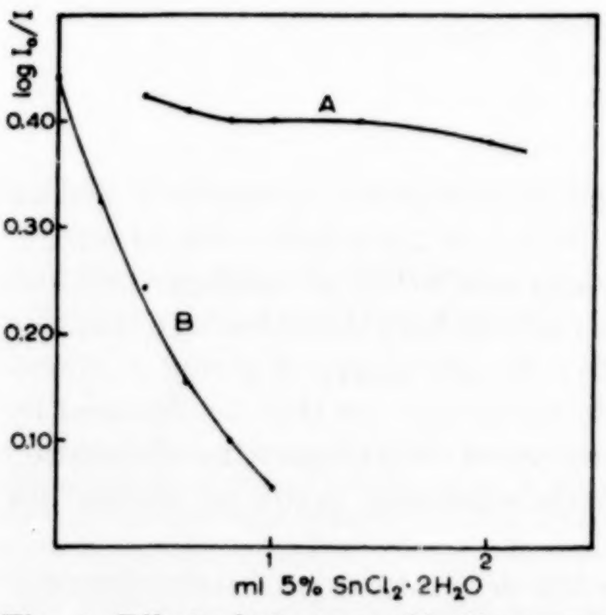

Fig. 2. Effect of stannous chloride concentration on color development with (*A*) 1,4-diphenylthiosemicarbazide, and (*B*) 2,4-diphenylthiosemicarbazide. Color developed in 80 ml 6 *N* hydrochloric acid; 5 ml chloroform for extraction; 20 μg Ru.

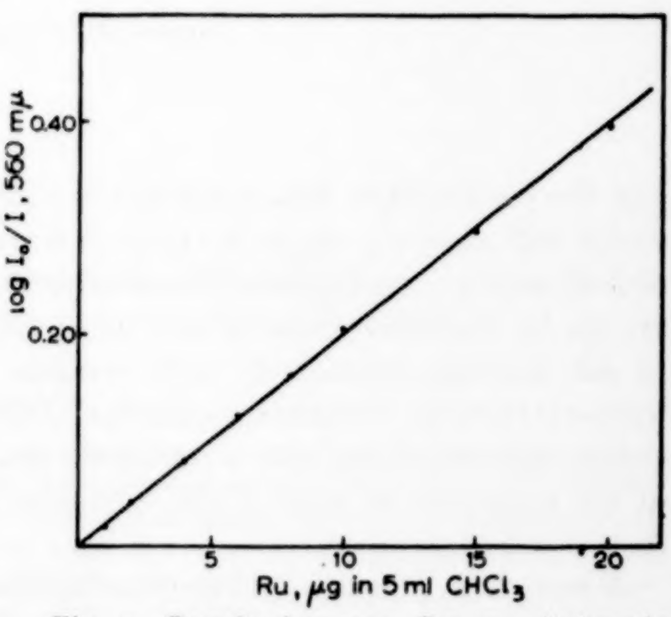

Fig. 3. Standard curve, Ru – 1,4-diphenylthiosemicarbazide.

μg Ru/cm² in chloroform for A = 0.001 at 560 mμ. The absorbance curve is shown in Fig. 1.

Stannous chloride is a suitable absorbent for ruthenium tetroxide in the determination of ruthenium with the 1,4 reagent. The composition of the ruthenium complex (or complexes) has not been established. Ruthenium is probably present in the +3 oxidation state.

Factors affecting color intensity and stability

The principal factors are the acidity, time of heating, and the stannous chloride concentration. The color develops slowly at low hydrochloric acid concentrations, more rapidly at higher, but fading occurs if the acidity is too great. The optimum hydrochloric acid concentration is 5.5–6.5 *N*. Full color development is obtained on heating for 10–15 min at 100°. The concentration of stannous chloride must be regulated fairly closely. In the range 0.8 to 1.4 ml of 5% $SnCl_2 \cdot 2\ H_2O$ in 80 ml of 6 *N* hydrochloric acid solution the color intensity remains constant (Fig. 2).

The absorbance is proportional to the ruthenium concentration at least as high as 20 μg Ru in 5 ml of chloroform. The precision of the procedure may be judged from Fig. 3. The results in Table I (obtained without separating ruthenium by volatilization of the tetroxide) show that a tenfold quantity of osmium can be tolerated but that rhenium interferes by giving a coloration.

TABLE I

DETERMINATION OF RUTHENIUM IN THE PRESENCE OF OSMIUM AND RHENIUM

Addition	*μg Ru*	
	taken	*found*
100 μg Os[a]	0	0.0
100 μg Os	1.0	1.0
100 μg Os	2.0	2.0
100 μg Os	5.0	4.9
140 μg Os	10.0	9.6
140 μg Os	20.0	19.8
100 μg Re[b]	0	5.5
100 μg Re	2.0	7.4

[a] As K_2OsCl_6
[b] As $KReO_4$

Separation of ruthenium

Volatilization of ruthenium as tetroxide has been adopted for its separation from iron and other constituents of the sample. A combination of sodium bismuthate and potassium permanganate as oxidizing agents was found to give satisfactory recoveries of ruthenium*. The large amount of ferrous iron in solution after dissolving iron meteorites in a non-oxidizing acid can best be oxidized with permanganate. The excess of the latter must be controlled. An excess greater than about 0.01 g leads to slightly low recoveries in the subsequent distillation. For example, 0.2 g of potassium permanganate in excess gave 90% recovery of 5 μg Ru, compared to 99% recovery with 0.01 g in excess (1 g sodium bismuthate also present in each). Oxidation of ferrous iron with excess chromic acid or cerium(IV), followed by addition of sodium bismuthate and distillation, gave poor recoveries of ruthenium; in the absence of ferrous iron initially, good recoveries could be obtained with either oxidizing agent in combination with bismuthate.

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* Unexpectedly, recoveries of 1 μg Ru (added as $(NH_4)_3RuCl_6$) amounted to 85–88% when 0.5 or 1 g $NaBiO_3$ was used alone as oxidizing agent. With 5 μg Ru, the recovery was 95% with bismuthate alone.

TABLE II

DETERMINATION OF RUTHENIUM AFTER DISTILLATION AS THE TETROXIDE

Addition	*μg Ru*	
	taken	*found*
1 g Fe(II)	0	0.0
1 g Fe(II)	1.0	1.0
1 g Fe(II)	2.0	1.85
1 g Fe(II)	5.0	4.8
1 g Fe(II)	20.0	19.8
1 g Fe(II), 0.4 g Ni	1.0	1.0
1 g Fe(II), 0.2 g Ni	5.0	5.0
1 g Fe(II), 100 μg Os, 100 μg Re	1.0	0.9
1 g Fe(II), 100 μg Os, 100 μg Re	2.0	1.9
1 g Fe(II), 100 μg Os, 100 μg Re	5.0	4.8
1 g Fe(II), 100 μg Os, 100 μg Re	8.0	8.0

Nitric acid, chlorine and other volatile strong oxidizing agents must not be present in the distillation mixture. They react with 1,4-diphenylthiosemicarbazide to give a yellow oxidation product. The meteorite sample is therefore treated with hydrochloric acid to dissolve the metal phase, chlorides are converted to sulfates by evaporation with sulfuric acid, and iron(II) is then oxidized with permanganate. Silicates and any other insoluble material are decomposed with sodium peroxide and the solution of the melt is combined with the acid portion.

Rhenium does not distil since its heptoxide is not appreciably volatile at the distillation temperature (~ 108°) of the procedure. Osmium will of course accompany ruthenium in the distillation, but this does not matter because of the tolerance of the reagent to this element.

The results in Table II demonstrate that satisfactory recoveries of microgram amounts of ruthenium can be obtained in the presence of much iron by the distillation method. A simulated determination of ruthenium in an iron meteorite, in which ruthenium was added to iron metal and the whole procedure carried through, gave recoveries of 95% (Table III). Further, the recovery of ruthenium from a stony meteorite was checked by adding 1.0 and 2.0 μg Ru to 2-g portions of the Ness County, Kansas, chondrite. Subtraction of the ruthenium present in the meteorite (1.44 μg in

TABLE III

DETERMINATION OF RUTHENIUM IN IRON[a]

μg Ru taken	1.0	2.0	5.0	8.0
μg Ru found	0.95	1.9	4.8	7.6

[a] Ru added as $(NH_4)_2RuCl_6$ to 1.0 g pure metallic iron which was dissolved in HCl. Chlorides were converted to sulfates by evaporating to fumes with sulfuric acid. Distillation of RuO_4 carried out as in procedure after oxidizing Fe(II) with slight excess of $KMnO_4 \cdot Na_2O_2$ fusion was made.

2 g) as determined by the proposed method, gave recoveries of 0.91 and 1.92 μg Ru, or 91 and 96%. From these results it appears that application of a +5% correction will bring the analytical values closer to the true value.

EXPERIMENTAL

Distillation apparatus

The apparatus described by Banks and O'Laughlin[3] is suitable. This consists of a 125-ml Erlenmeyer flask connected to a vertical condenser, the lower end of which reaches almost to the bottom of a 125-ml Erlenmeyer receiving flask, to which is attached a bubbler tube. Connections are made by means of ground glass joints. An inlet tube extends to the bottom of the distillation flask so that air can be passed through the apparatus to facilitate the volatilization of ruthenium tetroxide. Absorbing solution is placed in both the receiver flask and the bubbler. Doubtless similar distillation apparatus can be used as well, with an increase in distillation time if need be.

Special solutions

1,4-Diphenylthiosemicarbazide, saturated solution at room temperature in methyl alcohol. The reagent may be synthesized as follows, essentially according to the procedure of Walther[4]. Heat 40 g of thiocarbanilide with 70 g of phenylhydrazine on the water bath. Stir until the mixture suddenly crystallizes to a paste. Add 150 ml of methyl alcohol and stir the warm mixture well. Cool to room temperature, filter off the solid on sintered glass, and wash with small portions of methyl alcohol until the washings are colorless. Dry the product in a vacuum desiccator protected from strong light. M.p. 176°.

Stannous chloride, 5.0 g of $SnCl_2 \cdot 2\,H_2O$ in 100 ml of 6.0 N hydrochloric acid. Filter if not clear. Prepare fresh every 3 days.

Potassium permanganate, 1% aqueous solution.

Standard ruthenium solution. Ammonium chlororuthenate(IV) furnishes a convenient source of ruthenium*. Prepare a stock solution containing approximately 250 p.p.m. Ru by dissolving 0.20 g of ammonium chlororuthenate in 250 ml 1 N sulfuric acid. Dilute this solution with water to obtain a standard solution containing approximately 10 p.p.m. Ru. Determine the ruthenium content of the ammonium chlororuthenate by ignition to the metal in a stream of hydrogen in the usual way.

PROCEDURE

Iron meteorites

Dissolve 1 g of sample in 40 ml of 1 : 3 hydrochloric acid in a beaker, warming to hasten solution. Cool to room temperature and add 10 ml of concentrated sulfuric acid. Evaporate to fumes and continue fuming for 20 min. Cool to room temperature and add 35 ml of water. Warm to dissolve ferrous sulfate.

Filter the solution through a small porous porcelain crucible, the bottom of which has been covered with about 50 mg of aluminum oxide powder. Wash with a little water and transfer filtrate and washings to the original beaker. Place this on a steam bath to reduce the volume of the solution.

Dry the crucible in an oven and transfer the aluminum oxide and any insoluble material to a nickel crucible. Add to the latter about 0.5 g of sodium peroxide, which first has been used to clean the porcelain crucible. Heat the nickel crucible to low redness for 20–30 min, occasionally swirling the contents. Cool the crucible and dissolve the melt in 10 ml of water. Transfer the solution to a small beaker and cool in ice water. Add a slight excess of dilute sulfuric acid (cessation of gas evolution). Combine this solution, together with the few drops of sulfuric acid used to clean the nickel crucible, with the main portion, and continue the evaporation to a volume of about 40 ml.

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* Chlorides or sulfates of Ru(III) or (IV) can also be used.

Transfer the solution to the distilling flask, using 10 ml of water for rinsing so that the total volume is near 50 ml. Cool the flask in ice water and oxidize ferrous iron with a slight excess of permanganate. This is best done by adding finely powdered potassium permanganate in small portions with good mixing until the major portion of the ferrous iron has been oxidized, and completing the oxidation by adding 1% potassium permanganate solution. Add an excess of 1 ml of the latter. If too large an excess of permanganate is added, it can of course be destroyed with ferrous ammonium sulfate and a new adjustment made.

Add 1 g of sodium bismuthate to the flask, avoiding getting any on the neck of the flask. The volume of the solution at this point should be 50–60 ml. Immediately connect the flask to the condenser, which has been attached to the receiver flask containing 40 ml of 0.1% stannous chloride solution (add 1.0 ml 5% stannous chloride to 50 ml of 6.0 *N* hydrochloric acid and place 40 ml of this solution in the receiver and 10 ml in the bubbler). Heat the distillation flask with a burner and pass air through the system at a rate of two bubbles per second. After the solution has begun to boil and the condensate has reached the upper part of the condenser, continue the distillation for 5 min.

Disassemble the apparatus and transfer the absorbing solution (including that in the bubbler) to a 150-ml Erlenmeyer flask. Rinse the condenser and receiver with 30 ml of 6.0 *N* hydrochloric acid and add the rinsings to the Erlenmeyer. Add 3.0 ml of 1,4-diphenylthiosemicarbazide solution, mix, and heat the flask in a water bath at 100° for 12 min. Cool, transfer the solution to a separatory funnel, and rinse the flask with 20 ml 6 *N* hydrochloric acid, so that the total volume is close to 100 ml. Add 5.0 ml of reagent-grade chloroform and shake for one min. Allow the phases to separate, and, if the chloroform layer is not entirely free from water droplets, filter it through a very small rapid filter paper. Measure the absorbance of the extract against chloroform in a 1-cm cell at 560 mμ.

Establish the standard curve by taking 0, 5, 10, 15 and 20 μg of Ru(IV) and proceeding as described in the preceding paragraph. Run a blank through the whole procedure.

Silicate meteorites

Treat 2–2.5 g of crushed, representative sample with hydrochloric acid and evaporate with sulfuric acid as described under iron meteorites. Filter off the insoluble material in a porous porcelain crucible, wash, dry and fuse with 5 g of sodium peroxide in a nickel crucible. Then continue as described under iron meteorites.

ACKNOWLEDGEMENT

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SUMMARY

Ruthenium is determined in iron and silicate meteorites as the red-violet chloroform-extractable complex of 1,4-diphenylthiosemicarbazide, following volatilization as the tetroxide by oxidation with potassium permanganate and sodium bismuthate. Osmium need not be separated. From 0.5 to 15 p.p.m. (or more) of Ru can be determined in 1–2 g samples.

RÉSUMÉ

Les auteurs ont établi une méthode pour le dosage spectrophotométrique du ruthénium dans les météorites. Elle est basée sur la formation du complexe violet rouge, obtenu avec la diphényl-1,4-thiosemicarbazide. Le ruthénium est séparé au préalable par distillation de son tétroxyde (oxydation avec le permanganate de potassium et le bismuthate de sodium).

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur spektrophotometrischen Bestimmung von Ruthenium in Meteoriten. Sie beruht auf der Reaktion mit Diphenyl-1,4-thiosemicarbazid unter Bildung eines rotviolett gefärbten Komplexes. Zur Abtrennung wird Ruthenium zum Tetroxyd oxydiert und dieses abdestilliert.

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POLAROGRAPHIC DETERMINATION OF TRACES OF EUROPIUM IN MINERALS AND ORES*

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INTRODUCTION

Among the rare earth elements with high capture cross-sections, europium is most likely to be used in reactor components such as control rods, etc. Europium is generally present in negligible amounts in minerals rich in rare earths[1,2]. In nature it usually occurs in the bivalent state and consequently does not accompany the other lanthanides which are trivalent; instead it becomes concentrated in other minerals. A survey of the analytical data for most minerals reveals that results for europium are rarely reported.

Various volumetric[3] and spectrophotometric[4,5] determinations of europium have been described but none of these is suitable for determination of trace amounts of europium in minerals and ores.

In the polarographic study of rare earth metals[6,7] it has been shown that europium gives a wave at —0.67 V *vs.*S.C.E. in 0.1 *M* ammonium chloride supporting electrolyte; this is convenient for analysis because it is well separated from the half-wave potentials of the only other two rare earth elements which give waves, *viz.* samarium and ytterbium at —1.80 and —1.17 V respectively. Among the rare earths only these three elements are reduced from the trivalent to the divalent state. The reduction of the others proceeds from the trivalent state to the metal, with half-wave potentials between —1.75 and —1.95 V *vs.* S.C.E.

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* Presented to the Indian Standards Convention held in December 1959.

HOLLECK[6] proposed an indirect polarographic determination of europium which involved additions of known concentration of zinc to the rare earth solution and the calculation of the europium content from the difference in the wave heights obtained for zinc. LAITINEN AND TAIBEL[7] suggested that "since europium occurs only in very small concentrations in natural rare earth minerals, the usual analytical problem involves its determination in rare earth mixtures in which the europium concentration has been greatly increased by partial separation", but they did not indicate which special procedure was to be followed. They did not determine europium in minerals but used a synthetic mixture of europium and ytterbium oxides and determined europium polarographically, the percentage of europium oxide in the mixture being as high as 55.0% and 54.7%.

A better sensitivity in the determination of europium and ytterbium was obtained by POMEROY *et al.*[8] who used differential polarography. They proposed a modification of the Cambridge polarograph for derivative polarography and repeated the work of LAITINEN AND TAIBEL on the derivative polarograph. It was again not clear whether any partial separation of europium was made and what were the lowest limits in their determinations.

In the method described in this paper europium is determined in the total rare earths obtained from minerals without any further concentration of the element. The measurements were made at —0.67 V *vs.* S.C.E. in a supporting electrolyte of 0.1 *M* ammonium chloride on a "Du Bellay" polarograph.

EXPERIMENTAL

Standardisation

A linear relationship was obtained with 25 to 200 μg of europium in 25 ml of the solution containing 2.5 ml of 1.0 *M* ammonium chloride as supporting electrolyte.

Determination in minerals

In the case of minerals and ores 0.5 to 2 g of the sample was decomposed and the total rare earths were separated by conventional analytical procedures. The rare earth oxides obtained by ignition at 600° were dissolved in the minimum amount of

TABLE I

STANDARD ADDITION OF EUROPIUM TO DIFFERENT ORES

No.	*Sample*	*Weight of the sample g*	*Eu added μg*	*Total Eu expected μg*	*Eu found μg*	*% Difference*
1	Monazite	0.5	0.0	—	80	—
1a	Monazite	0.5	25	105	100	—4.76
1b	Monazite	0.5	50	130	130	0.0
1c	Monazite	0.5	75	155	160	+3.2
2	Crude rare earth oxide	0.5	—	—	160	—
2a	Crude rare earth oxide	0.5	200	360	360	0.0
2b	Crude rare earth oxide	0.5	400	560	560	0.0
3	Samarskite	1.0	—	—	75	—
3a	Samarskite	1.0	100	175	181	+3.5

hydrochloric acid and the solution was evaporated on a water bath. The residue was taken up with water, 2.5 ml of 1 *M* ammonium chloride were added and the volume was diluted to 25 ml in a measuring flask. A polarogram was then recorded.

For the polarographic determination europium had to be in the trivalent state and large amounts of lead, if present, had to be removed; for lead in an ammonium chloride supporting electrolyte gives a wave, the half wave potential being —0.45 V (approx.) *vs.* S.C.E. which is not far from the half wave for europium. Lead was removed by fuming the sample solution with sulphuric acid and separating the lead before the rare earths were separated. Any residual lead did not interfere in the determination.

In order to test the recoveries of europium in the separation process and the accuracy of the determination, the method of standard addition was adopted. The europium was added when the sample was dissolved before the separation of total rare earths. The results obtained with monazite and samarskite and a sample of crude rare earth oxides are given in Table I.

As can be seen from the Table, the accuracy of the determination in the range studied was better than 5%; with a 2-g sample, it is possible to determine as little as 10 p.p.m. in the sample. The results on monazite and samarskite samples showed europium contents of 0.016% and 0.0075% respectively.

ACKNOWLEDGEMENT

Our thanks are due to Shri M. M. Tillu for carrying out the preliminary separation of total rare earths from the samples studied.

SUMMARY

A method is described for the determination as little as 10–12 p.p.m. of europium in minerals and ores. After lead separation, the total rare earths are separated by conventional methods and the rare earth oxides are dissolved in hydrochloric acid. Europium gives a wave in 0.1 *M* ammonium chloride supporting electrolyte at —0.67 V *vs.* S.C.E. and there are no interferences. Europium is determined in monazite and samarskite.

RÉSUMÉ

Les auteurs ont mis au point une méthode polarographique pour le dosage de traces d'europium dans des minerais et en particulier en présence des autres terres rares (samarskite, monazite).

ZUSAMMENFASSUNG

Beschreibung einer polarographischen Methode zur Bestimmung von Europium in Mineralien (Monazit, Samarskit) in Gegenwart anderer seltener Erden.

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POLAROGRAPHIC DETERMINATION OF NICKEL, CHROMIUM AND TIN IN ZIRCALOY AND ZIRCONIUM METAL*

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INTRODUCTION

Zirconium and its alloys are finding ever-increasing use in nuclear reactors. Certain alloys of zirconium have become standard because of their resistance to corrosion and high temperature. The composition of zircaloy 2 is as follows: tin 1.4–1.6%; chromium 0.08–0.12%; iron 0.1–0.15% and nickel 0.04–0.06%. In zircaloy 3, iron and tin are of the order of 0.25% each.

Recently, ELWELL[1] has surveyed all the methods for the determination of different elements and impurities in zircaloy and zirconium metal. As regards the determination of chromium, nickel and tin in zircaloy by polarography, only the polarographic determination of tin[2] has been reported. The purpose of this paper is to describe suitable polarographic methods for the determination of these elements in zircaloy as well as in high purity zirconium metal.

EXPERIMENTAL

Instrument

A "DU Bellay" polarograph and an electronically operated thermostat were used. A mercury pool was used as anode and the temperature was kept constant at 30 ± 0.1°.

Reagents

Stannic chloride solution (0.1 *M*) was prepared from E. Merck G. R. stannic chloride and was standardised volumetrically with iodine. 0.01 *M* Solutions of potassium chromate and nickel chloride were prepared from Merck's G.R. quality salts. The nickel solution was standardised with dimethylglyoxime. The solutions (100 μg/ml) of ferric chloride, manganese sulphate, lead nitrate, titanium sulphate, ammonium vanadate and aluminium chloride were also prepared from E. Merck G.R. quality salts.

Preparation of the synthetic sample for analysis

Zirconium metal (5 g) was dissolved by first treating it with a few ml of 40% hydrofluoric acid in a platinum dish and fuming it with concentrated sulphuric acid. The solution was diluted to 100 ml after addition of 10 ml of concentrated sulphuric acid to prevent subsequent hydrolysis.

To an appropriate aliquot of the zirconium solution, the requisite amounts of chromium, nickel and tin (in the form of solutions) were added in the ranges of their percentages in zircaloy and then taken through separate procedures for estimation of each element as described below.

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* Presented to the Indian Standards Convention held in December 1959.

Determination of nickel

Supporting electrolyte and separation of zirconium

Pyridine–pyridine sulphate was used as the supporting electrolyte; this is known to give a very good wave for nickel. In addition, pyridine effectively precipitates zirconium. Ammonia, ethanolamine and ethylenediamine were also tried, but the separation of zirconium resulted in gelatinous precipitates which were difficult to wash. Ammonia for separation of zirconium is not suitable: the original solution contains sulphuric acid which gives ammonium sulphate in the filtrate. When ammonium sulphate is present in the supporting electrolyte, the height of the nickel wave decreases with increasing amounts of ammonium sulphate. Amongst the supporting electrolytes mentioned above, the wave-height for nickel in pyridine–pyridine sulphate solution is the highest.

Standard curves

To obtain a standard curve, 20–500 μg of nickel as nickel chloride solution was taken in different 25-ml flasks; 7 ml of 13 *M* pyridine and 1–2 ml of concentrated sulphuric acid was added and the volume made up to 25 ml. The half-wave potential of nickel is at —0.925 V *vs.* S.C.E.

In the case of samples, an aliquot equivalent to 0.25g (5 ml) of the sample (Zr-metal) was taken, 15 ml of water and 2–3 ml of concentrated sulphuric acid were added and zirconium was precipitated by addition of 14 ml of 13 *M* pyridine. The precipitate was filtered through No. 42 Whatman filter paper and washed with dilute pyridine solution (5% v/v). The filtrate and washings were collected in a 50-ml flask and the solution made up to the volume. Synthetic mixtures of zircaloy were prepared by adding the requisite amounts of elements present in the alloy. To one of the synthetic mixtures, the impurities generally present in zirconium metal were also added. Table I gives the results on synthetic samples.

TABLE I

DETERMINATION OF NICKEL IN SYNTHETIC SAMPLES

No.	*Wt. of sample as g of metal*	*Nickel added* μ*g*	*Nickel found* μ*g*	*Difference* %
1	0.25 alloy[a]	500	485	— 3
2	0.25 alloy[a]	200	188	— 6
3	0.2 alloy[a] with impurities[b]	200	188	— 6
4	0.5 metal[c]	20	17.5	—12.5
5	1.0 metal	75	71	— 5
6	1.0 metal	10	8.5	—15

[a] 0.25 g of synthetic alloy containing 0.104% chromium and 1.5% tin apart from zirconium.

[b] Iron (50 μg), aluminium (250 μg), titanium (25 μg) manganese (50 μg), lead (25 μg) were added as impurities to the synthetic alloy.

[c] The amount of nickel in the pure zirconium metal taken for analysis was 25 p.p.m. and was corrected for in calculating the results.

Determination of chromium

Advantage is taken of the fact that zirconium when treated with sodium peroxide is hydrolysed and precipitated. Chromium, if any, is oxidised to chromate which gives a good wave in a sodium hydroxide supporting electrolyte.

Standard curves for chromium were obtained as follows: 4 g of sodium peroxide were dissolved in water and the solution was boiled to remove excess of oxygen. It was then transferred to a 25-ml flask, measured quantities of chromate were added and the solution was made up to volume.

Synthetic samples containing appropriate aliquots of zirconium solution and varying amounts of chromium as indicated in Table II were used. To the solution (20 ml), 4 g of sodium peroxide were slowly added and the solution was boiled after addition of another 10–20 ml of water, cooled and then filtered. The precipitate of zirconium was washed thoroughly with dilute sodium hydroxide and the filtrate and washings were collected and concentrated to less than 25 ml. The solution was then transferred to a 25-ml flask and made up to volume. The polarogram was then recorded. Table II shows the results obtained for chromium on synthetic samples.

TABLE II

DETERMINATION OF CHROMIUM IN SYNTHETIC SAMPLES

No.	*Wt. of sample in g of metal*	*Cr added μg*	*Cr found μg*	*Difference %*
1	0.25 g alloy[a]	260	260	
2	0.25 g alloy[a]	130	126	—3
3	0.25 g alloy[a] with impurities[b]	130	130	
4	0.5 g metal[c]	20	20	
5	1.0 g metal	10	9	—10

[a] 0.25 g of synthetic alloy containing 0.08% nickel and 1.5% tin apart from zirconium.

[b] Impurities added are the same as in the case of nickel.

[c] The value of the chromium in the pure zirconium metal was 54 p.p.m. and was corrected for in calculating the results in Table II.

Determination of tin

The method of ALLSOPP AND DAMERALL[3] for the determination of tin in steels was applied. The method essentially consists of the precipitation of tin as stannic sulphide, ignition and subsequent fusion with bisulphate, leaching with 2 *N* hydrochloric acid, adding this solution to a 100-ml flask containing 21 g of ammonium chloride and 2 ml of 0.5% gelatin, making up to volume and recording the wave.

The earlier method of PORTER[2] for determination of tin in zircaloy by measuring the waves of stannous chloride without prior separation from the bulk of the solution was not used because of the difficulty of preventing oxidation of stannous chloride.

It is necessary to remove all oxygen from the reagents by passing nitrogen and to add iron powder to the solution to prevent oxidation of stannous tin. Although the method of ALLSOPP is rather lengthy no precautions are required and it is therefore more suitable for zircaloy.

The standard curves for tin were obtained by adding suitable quantities of tin to 100-ml volumetric flasks containing 21 g of ammonium chloride and 2 ml of 0.5% gelatin. Different quantities of tin were added to the synthetic sample and tin was determined by the above method. The results of this determination are shown in Table III.

A sample of zircaloy was analysed for nickel and chromium; the contents were found to be 0.063 and 0.12% respectively. The methods were also confirmed by additions of known amounts of nickel and chromium to the sample.

If the determination of tin in the range of 0.001% is required a 5-g sample of zirconium metal should be taken.

TABLE III

DETERMINATION OF TIN IN SYNTHETIC SAMPLES

No.	Wt. of sample g	% tin added	% tin found	Difference %
1	0.05 alloy[a]	1.74	1.68	−3.4
2	0.1 alloy[a]	1.74	1.68	−3.4
3	0.2 alloy[a]	0.50	0.47	−6.0
4	0.2 alloy[a]	0.25	0.275	+10.0
5	1.0 metal[b]	0.005	0.005	—

[a] The synthetic alloy sample contained 0.08% nickel and 0.104% chromium apart from zirconium.
[b] The tin content of the zirconium metal was less than 0.001% and has been corrected for.

SUMMARY

Polarographic methods are described for the determination of chromium, nickel and tin in zircaloy. The methods can be used to determine these three elements at the 10 p.p.m. level in pure zirconium metal.

RÉSUMÉ

Les auteurs ont mis au point une méthode polarographique pour le dosage du chrome, du nickel et de l'étain dans le zirconium et ses alliages.

ZUSAMMENFASSUNG

Es wird eine polarographische Methode beschrieben zur Bestimmung von Chrom, Nickel und Zinn in Zirkonium und dessen Legierungen.

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POLAROGRAPHY OF URANIUM IN THIOCYANATE MEDIUM

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INTRODUCTION

The polarography of uranium in various media has been reported by numerous workers. This paper reports the polarography of uranium in thiocyanate medium.

EXPERIMENTAL

Apparatus

Current–voltage curves were determined on a manual set up[1]. A H-type cell[2] was used in which a saturated calomel electrode (S.C.E.) served as a reference electrode. Before making polarographic measurements, all solutions were made air-free by bubbling nitrogen for about forty-five minutes. All experiments were carried out at 30 ± 0.5°. The diffusion currents reported were corrected for the residual current. The capillary used in these measurements had the following characteristics: m = 1.21 mg/sec and t = 5.0 sec in 0.1 N KCl (open circuit). A number of maximum suppressors was tried but only bromothymol blue (BTB) ($3 \cdot 10^{-3}\%$ in the final solution) was found satisfactory. All experiments were carried out at an ionic strength of 1.0 by the addition of requisite amounts of sodium perchlorate.

Chemicals

A stock solution of uranium perchlorate was obtained by fuming uranyl nitrate with perchloric acid and diluting to a known volume. The solution was standardized by the standard gravimetric method.

All chemicals used were AnalaR grade.

RESULTS

c–v curves

Fig. 1 gives the c–v curves for uranyl ion both in the presence and absence of thiocyanate. The acidity was 0.4 M in perchloric acid. Two waves were obtained in thiocyanate medium, the first corresponding to a 2-electron reduction of +6 to +4 uranium and the second to a 1-electron reduction of +4 to +3 as will be shown later.

In the text, $E'_{\frac{1}{2}}$ and $E''_{\frac{1}{2}}$ represent the half-wave potentials of the first and second wave respectively and i'_d and i''_d are the corresponding diffusion currents. i_t is the total diffusion current.

Half-wave potentials

The dependence of the half-wave potentials of the two waves on the hydrogen ion concentration was studied by varying the amounts of perchloric acid, the thiocyanate concentration being kept at 0.2 M. The results are given in Table I.

TABLE I

EFFECT OF ACID CONCENTRATION ON $E_{\frac{1}{2}}$

U = 1 mM, $NaClO_4 + HClO_4$ = 0.8 M, NH_4CNS = 0.2 M, BTB = $3 \cdot 10^{-3}\%$

Perchloric acid M	$E'_{\frac{1}{2}}$ *V vs. S.C.E.*	*Slope for first wave V*	$E''_{\frac{1}{2}}$ *V vs. S.C.E.*	*Slope for second wave V*
0.2	−0.146	0.034	—	—
0.3	−0.130	0.034	−0.892	0.062
0.4	−0.113	0.033	−0.892	0.064
0.46	−0.106	0.035	−0.894	0.068
0.5	−0.098	0.033	−0.890	0.065

According to HEYROVSKY-ILKOVIC[3], the potential at any point on the polarographic wave is given by

$$E_{d.e} = E_{\frac{1}{2}} - \frac{0.059}{n} \log \frac{i}{i_d - i} \tag{1}$$

A plot of log $i/(i_d - i)$ vs. $E_{d.e}$ (Fig. 2) gave straight lines for the two waves. The slopes for the first and second wave were 34 mV and 65 mV indicating a 2-electron and 1-electron reduction respectively.

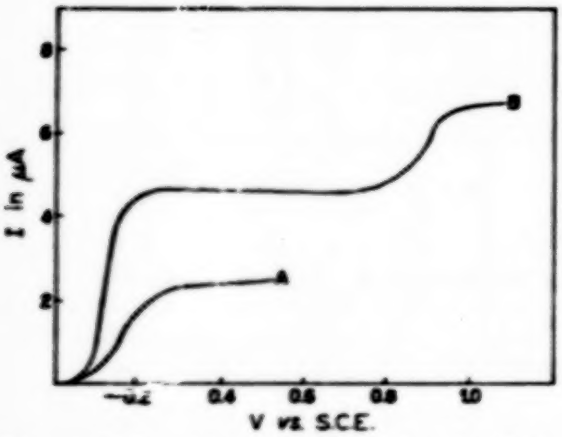

Fig. 1. Polarogram of uranyl ion in thiocyanate: U — 1 mM, $HClO_4$ — 0.4 M, $NaClO_4$ — 0.4 M, BTB — $3 \cdot 10^{-3}$%, NH_4CNS — (A) 0 M, (B) 0.2 M.

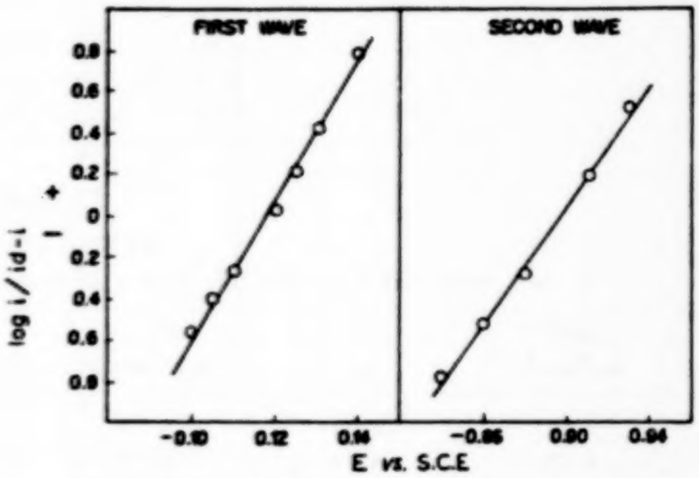

Fig. 2. Test of reversibility: log plot for equation (1).

Effect of thiocyanate concentration

Further experiments were carried out at an acid concentration of 0.4 M. Table II gives the effect of thiocyanate concentration on the two waves.

TABLE II

EFFECT OF THIOCYANATE CONCENTRATION

U = 1 mM, $HClO_4$ = 0.4 M, $NaClO_4$ + NH_4CNS = 0.6 M, BTB = $3 \cdot 10^{-3}$%

CNS^- concentration M	*First wave*			*Second wave*		
	$E'_{\frac{1}{2}}$ *V vs. S.C.E.*	*Slope* *V*	i_d' *at* −0.5 *V* *μA*	$E''_{\frac{1}{2}}$ *V vs. S.C.E.*	*Slope* *V*	i_t *at* −0.98 V *μA*
0	—	—	2.54	—	—	6.90
0.05	−0.111	0.034	4.49	−0.855	0.068	6.80
0.15	−0.112	—	4.61	−0.861	0.061	6.84
0.2	−0.113	0.033	4.61	−0.892	0.064	6.80
0.3	−0.117	0.031	4.64	−0.896	0.067	6.80
0.35	−0.118	0.030	4.66	−0.896	0.067	6.84
0.4	−0.115	0.035	4.61	−0.898	0.063	6.81

Effect of other factors:

(A) temperature

The temperature coefficient was determined by measuring the diffusion currents at different temperatures (Table III) and was found to be[4] of the order of +1.3%. The effect was also studied at a lower concentration of thiocyanate (0.01 M) where

i_d' had not reached the constant value of 4.62 μA; the temperature coefficient was found to be of the same order.

TABLE III

EFFECT OF TEMPERATURE ON THE DIFFUSION CURRENTS

U = 1 m*M*, $HClO_4$ = 0.4 *M*, $NaClO_4$ = 0.4 *M*, NH_4CNS = 0.2 *M*, BTB = $3 \cdot 10^{-3}$%

Temperature °C	i_d' *at* −0.5 *V vs. S.C.E.* μA	i_t *at* −0.98 *V vs. S.C.E.* μA	*Temperature coefficient* % *for*	
			i_d'	i_t
30	4.61	6.81	—	—
55	6.30	9.5	1.3	1.3
65	6.95	10.4	1.2	1.2

TABLE IV

EFFECT OF *m* AND *t*

U = 1 m*M*, $HClO_4$, $NaClO_4$ = 0.4 *M* each, NH_4CNS = 0.2 *M*, BTB = $3 \cdot 10^{-3}$%

$m^{2/3}t^{1/6}$ $mg^{2/3}sec^{-1/2}$	i_d' μA	$D_{UO_2^{+2}}$ $\times 10^5\ cm^2sec^{-1}$	$\frac{i_d'}{cm^{2/3}t^{1/6}}$	i_d'' μA	$\frac{i_d''}{cm^{2/3}t^{1/6}}$
1.41	4.32	0.64	3.06	2.16	1.53
1.49	4.62	0.66	3.10	2.26	1.51
1.29	3.91	0.63	3.03	2.02	1.56

(B) m and t

The diffusion currents of the two waves were measured with different capillaries and the ratio of i_d to $cm^{2/3}t^{1/6}$ was found to be constant within the limit of experimental error (Table IV).

(C) Concentration of uranium

The diffusion currents of the two waves were measured at different concentration of uranium and were found to be proportional (Table V).

TABLE V

EFFECT OF CONCENTRATION OF URANIUM

Capillary characteristics: $m^{2/3}t^{1/6}$ = 1.41 $mg^{2/3}$ $sec^{-1/2}$, NH_4CNS = 0.2 *M*, $HClO_4$, $NaClO_4$ = 0.4 *M* each, BTB = $3 \cdot 10^{-3}$%

Concentration of uranium m*M*	i_d' μA	i_t μA	i_d'' μA	i_d'/C	i_d''/C
2.0	8.75	12.82	4.07	4.38	2.04
1.0	4.32	6.48	2.16	4.32	2.16
0.5	2.14	3.20	1.06	4.28	2.12
0.1	0.44	0.66	0.22	4.40	2.20

DISCUSSION

First wave

Uranyl ion in the presence of thiocyanate gave a polarogram (Fig. 1) consisting of two waves. The first wave gave a slope of 0.033 V for the log plot for equation (1) indicating a two-electron reduction (Tables I and II). The shift of $E_{1/2}'$ to more positive potentials with increase in acid concentration (Table I) suggested the dependence of the first electrode reaction on hydrogen ion concentration. The reaction might be written as

$$UO_2^{+2} + 4\,H^+ + 2\,e \rightleftharpoons U^{+4} + 2\,H_2O \tag{2}$$

Or in the presence of excess thiocyanate, the general form of the equation would be

$$UO_2(CNS)_p^{(2-p)+} + 4\,H^+ + 2\,e \rightleftharpoons UCNS_q^{(4-q)+} + (p-q)\,CNS^- \tag{3}$$

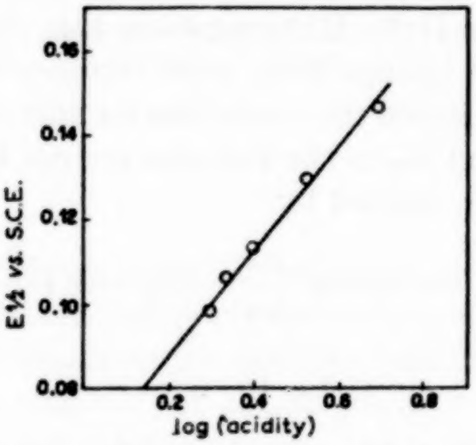

Fig. 3. First wave: log (acidity) *vs.* $E_{\frac{1}{2}}$.

The potential of the dropping electrode[3,5] at any point on the polarogram is expressed by

$$E_{d.e} = E^\circ + \frac{4RT}{nF} \ln a_{H^+} - \frac{RT}{nF} \ln \frac{i}{i_d - i} - \frac{(p-q)}{n} \frac{RT}{F} \ln a_{CNS^-} \tag{4}$$

It follows that at a particular concentration of thiocyanate, a plot of $E_{\frac{1}{2}}$ *vs.* log (acidity) should give a straight line with slope equal to $4RT/nF$ (Fig. 3). A slope of 0.123 V was obtained against a theoretical slope of 0.12 V at 30°. The activity term was neglected.

$E'_{\frac{1}{2}}$ remained unaffected at —0.114 ± 0.003 V (*vs.* S.C.E.) with the change in concentration of thiocyanate (Table II). Hence, the value of $p - q$ was equal to zero. The dependence of the first wave on hydrogen ion concentration and the fact that the slope of the log plot of equation (6) was equal to the theoretical slope showed that under the conditions studied the first wave was due to the reduction of uranyl thiocyanate complex to U^{+4} ion. The U^{+3} – U^{+4} couple was shown to be reversible at the dropping mercury electrode; the ionic species were U^{+3} and U^{+4} in acid solutions[6].

The first wave was found to be independent of the capillary characteristics (Table IV). The temperature coefficient (Table III) and the i'_d linearity with concentration of uranium (Table V) were also as expected.

For the diffusion currents obtained for a 1 m*M* solution of uranium with different capillaries and for a value of *n* equal to 2, the diffusion coefficient for UO_2^{+2} calculated from the ILKOVIC equation

$$i_d = 605\, n\, D^{\frac{1}{2}}\, cm^{\frac{2}{3}} t^{\frac{1}{6}} \tag{5}$$

was 0.65 ± 0.02 · 10^{-5} cm² sec⁻¹. This was in fair agreement with the values reported[7-9] and was satisfactory evidence for a two-electron reduction.

Second wave

The half wave potential of the second wave remained unaffected with acid concentration at —0.89 V *vs.* S.C.E. (Table I). With 0.4 M perchloric acid, $E_{\frac{1}{2}}''$ remained constant with change in thiocyanate concentration. i_d' and $E_{\frac{1}{2}}''$ were constant above a thiocyanate concentration of 0.15 M. The total height of the two waves was constant at 6.86 μA; i_d' was 4.62 μA and i_d'' was 2.26 μA. The ratio of 2 to 1 indicated a two- and one-electron reduction respectively. The slope for the log plot (Tables I and II) was 0.065 V indicating a one-electron reversible reduction.

The formal potential of the $U^{+3} - U^{+4}$ couple in this medium was calculated. In general, diffusion coefficients change little with changes in salt concentration and their ratios change even less; hence the correction for this effect was neglected. Since the activity coefficients f_{ox} and f_{red} of the two ions are not known with any accuracy, a formal electrode potential is defined by

$$E_f = E^\circ + 0.059 \log \frac{f_{ox}}{f_{red}} = E_{\frac{1}{2}} - \log \left(\frac{D_{red}}{D_{ox}} \right)^{\frac{1}{2}} \qquad (6)$$

For the reaction

$$U^{+3} \rightleftharpoons U^{+4} + e \qquad (7)$$

the half wave potential of the second wave was taken as —0.893 ± 0.003 V (*vs.* S.C.E.). The formal potential was +0.65 V. This value compared well with the values of +0.63 V in 1.0 M $HClO_4$,[6] +0.68 V[10] and +0.63 V previously reported[11].

ACKNOWLEDGEMENT

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SUMMARY

Uranyl ion in the presence of thiocyanate gave two polarographic waves, the first corresponding to a two-electron reduction of UO_2^{+2} to U^{+4} and the second corresponding to a one-electron reduction of U^{+4} to U^{+3}. The dependence of the two waves on acid concentration, temperature, etc., was studied.

RÉSUMÉ

Une étude a été effectuée sur le comportement polarographique de l'uranium (UO_2^{+2}) en présence de thiocyanate; on observe deux ondes dues à la réduction de UO_2^{+2} en U^{+4} et de U^{+4} en U^{+3}.

ZUSAMMENFASSUNG

Bei der polarographischen Bestimmung von Uranyl-Ion (UO_2^{+2}) in Gegenwart von Thiocyanat erhält man zwei Wellen, von denen die erste der Reduktion von UO_2^{+2} zu U^{+4} und die zweite der Reduktion von U^{+4} zu U^{+3} entspricht.

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PYROHYDROLYTIC SEPARATION OF FLUORIDES FROM CATALYSTS BY USE OF AN OXY-HYDROGEN BURNER

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Coinciding with the rapid advancement of reforming technology within the petroleum industry, there has been a correspondingly intensified interest in catalyst composition and structure. This has emphasized the need for rapid catalyst analyses not only for adequate refinery process control, but also in research activity where many process variables are studied. Fluoride determination has heretofore been one of the major obstacles to rapid catalyst evaluation because of the nature of the chemical bonds and the geometry of the crystalline structure of catalytic materials.

The concept of pyrohydrolysis is not new, the essential technique having been reported by FREMY[1] in 1856. Early activities, which have been reviewed by WARF *et al.*[2], while concerned almost exclusively with qualitative observations and thermodynamic data, clearly indicated the analytical potentialities of the technique. However, it was not until the advent of atomic research and the preparation of large quantities of inorganic fluorides that these potentialities were exploited[2,3].

WARF[3] and later WARF, CLINE AND TEVEBAUGH[2] used a steam generator in conjunction with a resistance furnace and platinum combustion reactor and boat to obtain the fluoride content of many inorganic materials. Addition of accelerators was necessary in many instances to produce quantitative results in reasonably short periods of time. Of secondary interest was the pyrohydrolysis of inorganic chlorides and bromides. An all-metal refinement of the apparatus was introduced by SUSANO, WHITE AND LEE[4], and later modified by GAHLER AND PORTER[5] for the pyrohydrolytic determination of chlorides in titanium sponge. Radioactive samples were studied by LEE, EDGERTON AND KELLY[6] in an apparatus designed specifically for the purpose. The precision of the pyrohydrolytic technique applied to uranyl fluoride and uranium tetrafluoride was studied by HIBBITS[7]. Elimination of the somewhat cumbersome steam generator was reported by POWELL AND MENIS[8] who used a continuous flow of oxygen containing traces of moisture.

GAMBLE, PRICE AND JONES[9] adapted the basic method of WARF to the somewhat more difficult problem of determination of fluorides in silica-alumina catalysts. A major departure from previously employed apparatus was reported by CONRAD, EVANS AND GAYLOR[10] who employed a high frequency induction furnace, using silica as an accelerator.

Investigations carried out in this laboratory indicate that procedures using resistance furnaces in conjunction with steam or moist oxygen are not competitive with the technique involving a basic fusion followed by distillation according to WILLARD AND WINTER[11] when applied to commercial type silica–alumina catalysts. Although comparable results may be obtained, time cycles are usually prohibitive in the absence of added accelerators. Using the reported high frequency induction furnace method[10], quantitative results could not be obtained on typical petroleum catalysts.

All of the reported pyrohydrolytic techniques have certain disadvantages when employed for routine use on catalytic materials. The steam generator–resistance furnace combination is cumbersome. Use of platinum and special all-metal apparatus requires substantial monetary outlays and elaborate fabrication facilities. When steam is used, careful manipulation and control is required to prevent back diffusion of hydrogen fluoride into the generator. Addition of accelerators is somewhat tedious and time consuming.

The WICKBOLD type oxy–hydrogen burner[12] is now commercially available at relatively low cost[13]. It provides an excellent means of utilizing the inherent advantages of the pyrohydrolytic technique while simultaneously eliminating many disadvantages of other methods. The burner provides a combined source of heat and water vapor in the presence of excess oxygen. Investigation of these potentialities resulted in the development of a new pyrohydrolytic separation technique, adaptable to the separation of fluoride from catalysts and which is suitable for routine use by technicians.

APPARATUS

The Wickbold apparatus[12] was modified by insertion of a special quartz combustion tube as indicated in Fig. 1. The Wickbold suction burner and water-jacketed combus-

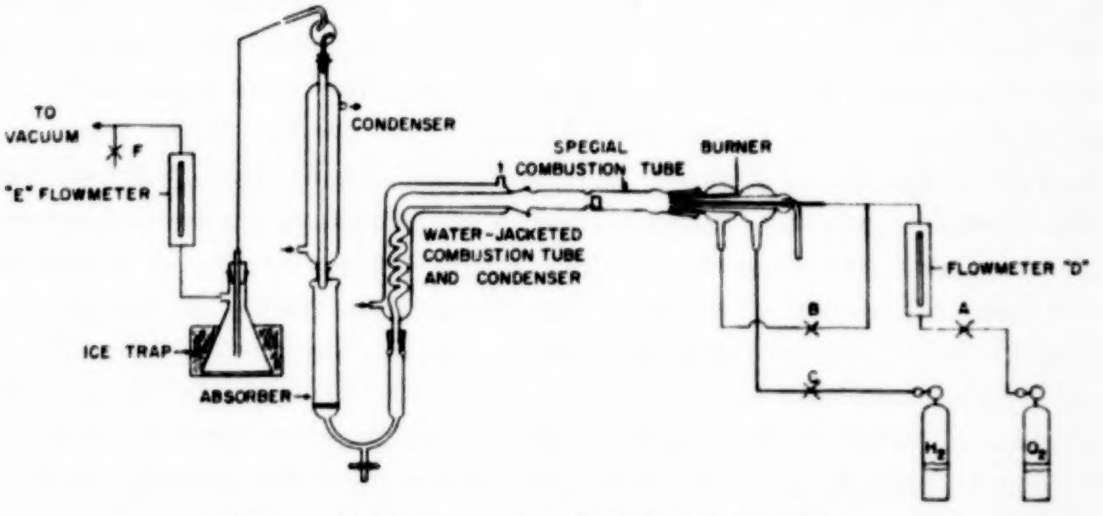
TO VACUUM
F
"E" FLOWMETER
CONDENSER
SPECIAL COMBUSTION TUBE
BURNER
WATER-JACKETED COMBUSTION TUBE AND CONDENSER
FLOWMETER "D"
B
A
C
ICE TRAP
ABSORBER
H_2
O_2

Fig. 1. Diagram of pyrohydrolysis apparatus.

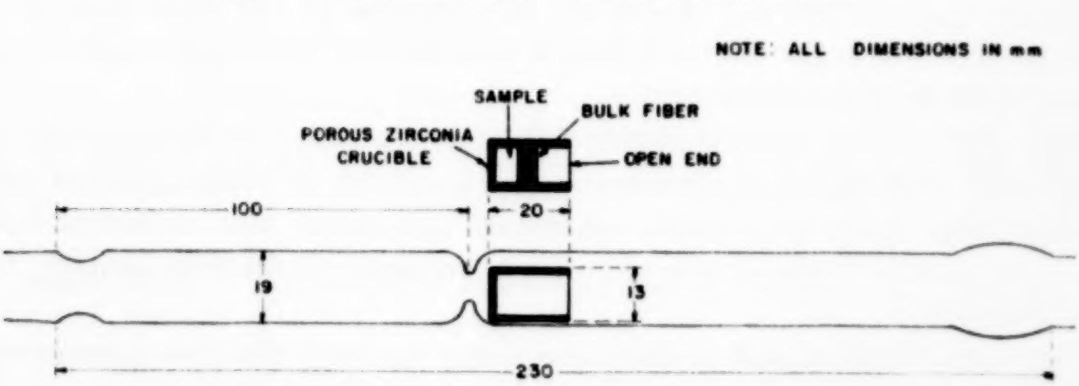
NOTE: ALL DIMENSIONS IN mm
SAMPLE
BULK FIBER
POROUS ZIRCONIA CRUCIBLE
OPEN END
100
20
19
13
230

Fig. 2. Special combustion tube and sample holder.

tion tube with condenser, both fabricated from clear fused quartz, were purchased from the Amersil Company, Hillside, New Jersey.

A special quartz combustion tube and a zirconia sample holder are required and are illustrated in Fig. 2. The porous sample holder, which permits free flow of superheated oxygen and water vapor from the flame, was designed specifically for this application and fabricated by the Laboratory Equipment Corporation, St. Joseph, Michigan.

The sample was held firmly in position by the use of F–100 Refrasil bulk fiber which was purchased from the H. I. Thompson Fiber Glass Company, Los Angeles, California. The absorber used in an ASTM lamp combustion procedure[14] was modified to fit the apparatus, and a bottom stopcock inserted for convenient withdrawal of the solution. Oxygen and hydrogen were used from cylinders, without purification. Lines were equipped with flowmeters and valves as indicated in Fig. 1.

PROCEDURE

The sample, equivalent to at least 1 mg of fluoride, was charged to the sample holder followed by a layer of the bulk fiber. The combustion tube, with the sample container located as shown in Fig. 2, was inserted into the assembly. The absorber, containing about 15 ml of approximately 0.1 N sodium hydroxide solution, was placed in position. Prior to inserting the burner in the assembly, vacuum was applied to the system and regulated to permit a flow rate of 20 l per min through flowmeter E. With valves A and C closed, the reducing valves on the oxygen and hydrogen cylinders were regulated to 4 psig. The hydrogen valve C, was opened slightly and the burner ignited. With valve B fully open, valve A was adjusted to permit a flow of about 16.7 l of oxygen per min through flowmeter D. Final adjustment of oxygen flow, at this rate, was made while simultaneously adjusting the hydrogen flow rate to produce a flame about 1 cm in length. The burner was then inserted into the special combustion tube, and the hydrogen flow increased to produce a flame 4–5 cm in length. By means of valve B, the excess oxygen passing through the burner was decreased causing more oxygen to jet through the center orifice of the burner. The resultant long narrow flame heats the sample to an intense white heat. The reduced oxygen flow during actual operation was estimated at approximately 11 l per min. After five minutes, the hydrogen valve was closed, the burner removed from the assembly, and the oxygen valve closed. The vacuum was disconnected and the contents of the absorber filtered through Whatman No. 41 filter paper. Fluorides were determined spectrophotometrically, using the method of MEGREGIAN[15] without prior distillation.

DISCUSSION

A review of the various methods for elimination of interferences and ultimate fluoride analysis is considered beyond the scope of this paper. In order to evaluate the new pyrohydrolytic technique, however, it was necessary to select a referee method which would eliminate any probable interferences and provide an independent means of sample preparation. Basic fusion is considered standard technique for obtaining dissolution of alumina and silica base catalyst materials, and was used in conjunction with the distillation method of WILLARD AND WINTER[11], which has been accepted almost universally as an ideal means of eliminating interferences in the subsequent fluoride analysis. Furthermore, a background consisting of years of experience with experimental and commercial catalysts using the fusion–distillation technique was available. Fluorides were determined spectrophotometrically[15] regardless of whether the fusion–distillation or pyrohydrolytic technique was used.

TABLE I

COMPARISON OF PYROHYDROLYSIS AND FUSION–DISTILLATION ON EXPERIMENTAL CATALYSTS

Catalyst type	*Fluorine found*	
	Distillation fusion	*Pyrohydrolysis*
Fresh reforming—Al_2O_3	0.55	0.55; 0.55
Fresh cracking—Al_2O_3-SiO_2 base	2.87	3.02; 3.03
Spent cracking—Al_2O_3-SiO_2 base	0.35	0.32; 0.37
Fresh cracking—SiO_2–MgO base	1.75	1.79; 1.80
Fresh hydrogenation—Al_2O_3 base	1.51	1.52; 1.56
Spent hydrogenation—Al_2O_3-SiO_2 base	1.29	1.45; 1.46
Spent hydrogenation—Al_2O_3-SiO_2 base	0.91	1.00; 0.94

Results from the pyrohydrolysis of various experimental petroleum catalysts are shown in Table I. Comparison of the values with the fusion–distillation technique indicates slightly higher recovery by pyrohydrolysis in most instances. For purposes of confirming the higher values, several absorber solutions were divided in two parts; one portion was subjected directly to the photometric finish and the other portion distilled prior to the photometric finish. In no instance was any difference in fluoride values observed before and after the distillation. The slightly higher values obtained by pyrohydrolysis confirms the belief that, in some samples, the fusion–distillation technique was not quantitatively liberating all of the fluorides. The order of magnitude of the discrepancy, however, is not usually considered to be of practical significance.

The general agreement of values obtained by the two methods indicates no appreciable interference from any of the catalyst bases nor from platinum, magnesium, cobalt, molybdenum, chlorine, sulfur, and various other metals commonly used in the form of supported catalysts. The method was also found to be equally applicable to both fresh catalysts and spent catalysts containing carbonaceous material. No blank could be obtained on the gas streams. Over a range of fluoride concentration of 0.3 to 3% and covering several hundred analyses, a standard deviation of about 0.04% has been estimated for the new method.

Inasmuch as materials of interest usually contain Al–F bonds, it was logical to expect that the method should be applicable to aluminum fluoride. Analysis of a sample of aluminum fluoride by the pyrohydrolytic and fusion–distillation techniques indicated an assay of 88.7% and 88.0% respectively, calculated as $Al_2F_6 \cdot 7H_2O$. Although the aluminum fluoride was of reagent grade quality, semi-quantitative x-ray diffraction studies indicated quantities of $Al_2O_3 \cdot 3H_2O$ present in the material in amounts sufficient to account for the difference.

Reports by WARF and others on the difficulty of pyrohydrolyzing calcium fluoride in the absence of accelerators promoted a brief investigation. Two samples obtained from the National Bureau of Standards—"fluorspar" certified to contain 94.83% calcium fluoride and "opal glass" certified to contain 10.48% calcium oxide and 5.72% fluoride—were subjected to a 15-min period of pyrohydrolysis with virtually quantitative recovery of fluoride. Inasmuch as calcium fluoride is not of primary interest in reforming catalyst technology, detailed studies on this phase were not conducted. It was obvious, however, that the procedure could be adapted for materials of this type.

TABLE II

TIME REQUIREMENTS FOR VARIOUS CATALYST TYPES

Heating time, min	*Alumina*	*Fluorine found, %*	
		Silica–magnesia	*Experimental silica–alumina*
1	0.48	1.61	2.82
2	0.56	1.81	2.90
4	0.58	1.72	2.98
8	0.59	1.80	2.97
15	0.59	1.86	3.01

A brief study of time requirements for the pyrohydrolysis of four types of catalytic materials was conducted (Table II). The recovery of fluorine does not appear to be significantly affected until the heating period is reduced to one minute. Unfortunately, the absence of a convenient means of measuring the sample temperature complicates any thermodynamic calculations which could be applied to this system. It appears, however, that the recovery of fluorides is primarily a function of temperature rather than time. The temperature of the oxy-hydrogen flame has been estimated to be 2690° and 2810° by two investigators[16,17]. From the appearance of the Refrasil bulk fiber in conjunction with measurements on an optical pyrometer, it is estimated that under the conditions cited, a sample temperature of approximately 1400° is attained.

Several types of sample holders were evaluated. A boat with an open top, although covered with the bulk fibers, was unsatisfactory because of mechanical loss of sample resulting from the flow of excess oxygen. Sample containers fabricated from quartz are satisfactory, but care must be taken to avoid overheating and subsequent melting. A later refinement involved the use of the recommended zirconia sample holder. If holders fabricated from quartz are employed, it is advantageous to use an auxiliary burner (Bunsen type) placed below the sample holder. In this case, the size of the oxy-hydrogen flame may be diminished slightly and the life of the holder extended.

The time required to prepare a sample for the final measurement of fluoride is of the order of only ten minutes. This, when compared to about three hours for a fusion-distillation procedure, simplifies many problems associated with process research and control.

The extreme simplicity of the new pyrohydrolytic technique makes it readily adaptable to routine use at the technician level. The operation is quite safe when the usual precautions regarding the use of hydrogen are observed. The use of an antiflash back device in the hydrogen line, a safety shield, and a reliable source of vacuum is recommended.

Other potential applications of pyrohydrolysis using the oxygen–hydrogen flame, currently being explored, include pyrohydrolysis of the other halides. Techniques other than hydrolysis, such as volatilization of certain components in solid substances are also being considered.

SUMMARY

A new pyrohydrolytic technique has been developed. The procedure utilizes an oxy-hydrogen burner as a combined source of heat and water vapor for high temperature hydrolysis of fluorides in catalytic materials. Fluorides in typical petroleum catalysts are quantitatively liberated in less than 5 min, without the use of added accelerators and without resorting to fusion or distillation. Results obtained are comparable to the fusion–distillation technique with a standard deviation of not more than 0.04 % over the range of concentration investigated: 0.3 to 3%. Indications are that materials of much higher fluoride content may also be handled in the same manner.

RÉSUMÉ

Une nouvelle technique pyrohydrolytique a été élaborée. Elle peut être utilisée, dans l'industrie, du pétrole, pour la séparation des fluorures dans des substances de catalyse.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Abtrennung von Fluorid aus Katalysatoren durch Pyrohydrolyse. Die Substanz wird der Atmosphäre einer Knallgasflamme ausgesetzt und das Fluorid anschliessend spektrophotometrisch bestimmt. Weitere Anwendungsmöglichkeiten dieser Methode werden untersucht.

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THE DETERMINATION OF SULFHYDRYL GROUPS IN REDUCED HAIR KERATIN

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INTRODUCTION

One of the distinguishing characteristics of the keratins is the presence of the reducible disulfide bond, and considerable activity in such fields as wool processing and hair chemistry has been directed to analytical means for estimating the disulfide and sulfhydryl groups. Because of the interest in these laboratories in the reduction of hair with mercaptans such as thioglycollic acid, the need for a rapid and precise method for determination of the sulfhydryl content of hair, preferably using intact, that is, nonhydrolyzed samples, is evident.

Earlier studies concerned with the determination of the disulfide and sulfhydryl groups in keratin involved a hydrolytic procedure for the liberation of the individual amino acids and a subsequent colorimetric measurement[1-6]. However, there is much controversy with respect to the specificity and quantitative nature of methods utilizing such an approach[7,8]. Other means of analysis have been proposed but they are not conveniently applicable. For example, the use of 1-(4-chloromercuriphenylazo)-naphthol-2[9-11] requires that the keratin be pulverized and reacted with the reagent for more than a day. Another reagent, iodosobenzoic acid, has been used to estimate the sulfhydryl content of denatured albumin and ovalbumin[12], but the technique was not applied to intact keratin samples. More recently, N-ethylmaleimide[13] and *p*-chloromercuribenzoic acid[8] have been used to estimate the sulfhydryl content of intact wool fibers. However, there is evidence presented that in both of these procedures these compounds are absorbed by the wool to some extent. Since the methods utilizing these chemicals, as well as the two mentioned previously, are indirect and are based on the decrease in concentration of reagent as a measure of sulfhydryl, loss of reagent by either absorption, adsorption, or in any other manner, could give rise to serious error.

BENESCH AND BENESCH[14] have used iodoacetamide for the quantitative determination of sulfhydryl groups in the soluble compounds cysteine, cysteinylglycine, and glutathione. Their method was based on the reaction

$$RSH + ICH_2CONH_2 \rightarrow RSCH_2CONH_2 + HI \qquad (1)$$

The analysis was completed by titrating the acid generated with standard base. Amounts of the order of 0.02 to 0.10 mequivs of material were determined. Since this procedure provides a direct measurement of the sulfhydryl content, an investigation was instituted to determine whether iodoacetamide could serve as a reagent for the determination of the sulfhydryl level of reduced human hair.

A direct application of the BENESCH method to hair was not considered practical for several reasons. It was almost certain that the reaction conditions suitable for the analysis of simple thiol-containing compounds would not be drastic enough to insure completeness of reaction between mercaptan groups in the insoluble protein and iodoacetamide. In addition, it was doubtful whether an acid–base titration could be conveniently applied to the desired low concentrations of interest, of the order of 0.0005 mequivs, particularly with buffering groups of the keratin protein being present.

It will be noted in reaction (1) above that iodide as well as hydrogen ion is liberated. The determination of sulfhydryl content via some quantitative measurement of iodide ion appeared to offer a better chance for the successful estimation in the microequivalent range. Potentiometric titrations of iodide ion with silver ion can be performed with good accuracy at low concentrations[15]. Therefore, this method of assay was chosen as the means of determining the amount of iodide ion liberated as a result of the iodoacetamide-reduced hair reaction.

To obtain samples of different sulfhydryl content, human hair was immersed in basic thioglycolate solutions of varied normality for different lengths of time. Such a treatment is known to convert the disulfide bond in keratin to thiol groups[16,17]. The use of thioglycolate reduction introduced the problem of the complete removal of the treatment solution since any reducing agent remaining on the hair would react readily with iodoacetamide and lead to erroneously high results. In addition to determining the conditions necessary to remove all of the thioglycolate, the following factors were considered:

(a) The time required for completion of the reaction between iodoacetamide and the mercaptan group in the reduced keratin;

(b) The reproducibility of the results for a given hair sample at different weight levels; and

(c) The stabilization of sulfhydryl groups in a sample so that reoxidation to the disulfide would not occur and consistent results for a given hair sample would be obtained over a period of time.

DEVELOPMENT OF METHOD

Preliminary

Preliminary experiments were made to determine the stability of iodoacetamide in basic solution for a time ranging from five minutes to several hours, an interval anticipated to be sufficient for complete reaction between reduced hair and iodoacetamide. For this purpose, 10.0-mg portions of iodoacetamide obtained from the Eastern Chemical Corporation, Newark, New Jersey, were placed into each of three 10-ml volumetric flasks. Clark and Lubs pH 10 borate buffer, containing potassium nitrate instead of potassium chloride, was added to the mark. The contents of the flask were shaken and, after five minutes, one hour, and two hours, a 5.00-ml aliquot was withdrawn by pipette and was transferred into a 50-ml beaker. The pH of the system was adjusted to approximately 7.5 by addition of three drops of 6 *N* nitric acid and solid sodium bicarbonate. The solution was then titrated with silver nitrate solution delivered from a 10-ml semimicro burette reading directly to 0.02 ml. The progress of the titration was followed potentiometrically, utilizing a Beckman Model G pH meter to measure the potentials. The electrodes employed were a Beckman silver indicator electrode and an isolated saturated calomel reference electrode. Contact between the two was made by means of a 1 M ammonium nitrate – 4% agar salt bridge. The silver solution used was 10^{-3} N, prepared daily as required by a 1 : 10 volumetric dilution of a standard 10^{-2} N solution. A blank value corresponding to approximately $1.8 \cdot 10^{-4}$ mequivs of silver ion was indicated for the one- and two-hour reaction times, whereas, $1.5 \cdot 10^{-4}$ mequivs of silver ion was required to titrate the sample which had reacted for five minutes. These results demonstrated that iodoacetamide could be used at pH 10 for at least two hours without appreciable hydrolysis. The iodide ion which was titrated could be accounted for by an appropriate blank value, slightly dependent upon the time of reaction at pH 10.

A similar experiment was carried out using iodoacetamide recrystallized from water. With this material, no iodide ion at all was found in solution after two hours in a pH 10 solution.

Reaction time study

Since the time required for the reaction between the sulfhydryl groups in hair and iodoacetamide to go to completion was not known, the amount of iodide ion liberated by a given hair sample as a function of reaction time was studied. For this experiment, a sample of human hair obtained from DeMeo Brothers, New York, was immersed for 30 min in 0.61 N ammonium thioglycolate solution which had been adjusted to pH 9.2 with ammonia and the excess thioglycolate was removed from the hair by three successive washings in hot glacial acetic acid. The sample was then cut into 1/8" lengths and dried in a vacuum oven at 110° for one hour. An appropriate weight was then placed into a 10-ml volumetric flask, 10.0 mg of iodoacetamide were introduced and pH 10 buffer solution was added to the mark. The contents of the flask were shaken, and after a given time interval, a 5.00-ml aliquot was transferred from the flask by means of a pipette. After pH adjustment, the solution was titrated with standard 10^{-3} N silver nitrate solution as previously described. The results of the experiment are shown in Table I. The data show that 15 min is insufficient time for the reaction to go to completion but that essentially constant results can be obtained if the reaction time is 30 to 120 min.

TABLE I

EFFECT OF REACTION TIME ON THE RESULTS FOR SULFHYDRYL LEVEL

High SH-level

Weight of hair mg	*Reaction time* min	*SH-level* mequivs/g
20.0	15	0.651
20.0	30	0.779
20.0	60	0.776
20.2	120	0.782

To determine whether a 30- to 60-min reaction time is sufficient for samples of low sulfhydryl content, for hair which is much less reduced and thus, less susceptible to the penetration of iodoacetamide, the above experiment was repeated with hair reduced for six minutes in 0.30 N ammonium thioglycolate. These samples were then extracted with glacial acetic acid for two hours in a Soxhlet extractor, dried, and treated as before. In this particular series, reaction times of 5, 30, 60, 90, and 120 min were used. These results are shown in Table II.

TABLE II

EFFECT OF REACTION TIME ON THE RESULTS FOR SULFHYDRYL LEVEL

Low SH-level

Weight of hair *mg*	*Reaction time* *min*	*SH-level* *mequivs/g*
26.9	5	0.084
25.6	30	0.138
24.4	60	0.134
28.1	90	0.138
28.4	120	0.138

Since these results agree with the others, in that essentially constant values are obtained after 30 min, a reaction time of 45 min was used in all subsequent experiments.

Thioglycolate removal

To obtain a true value for the sulfhydryl content of a thioglycolate-reduced hair sample, it was necessary that all of the treatment solution be removed from the fibers. The procedure used in the first part of the above experiment, washing with three portions of hot glacial acetic acid, may not have removed the last traces of thioglycolate and, what is more important, some oxidation of the keratin sulfhydryl may have occurred during the rinsings. In an attempt to minimize or eliminate oxidation, and still accomplish the complete removal of thioglycolate solution, samples were extracted with glacial acetic acid in a Soxhlet extractor. In this experiment, three portions, each approximately 100 mg, of a given hair sample were each placed into a 1 × 5 cm extraction thimble, and the thimble was then set into a micro Soxhlet apparatus. The first sample was analyzed after one hour of extraction, the second after two hours, and the last one after three hours. Highly reduced hair was used in this experiment because it was thought that the greatest amount of residual thioglycolate would be present in this case. As a control, the behavior of hair containing a low sulfhydryl level was also observed.

The data obtained in the above experiments are shown in Table III. It is apparent that the extractions of one and two hours yielded essentially the same results, whereas, lower values were obtained when three-hour extractions were utilized. The reason for the difference could be due to some reoxidation of keratin sulfhydryl

TABLE III

EFFECT OF SOXHLET EXTRACTION WITH GLACIAL ACETIC ACID ON THE SULFHYDRYL LEVEL OF REDUCED HAIR

Extraction time *h*	*SH-level*[a] *mequivs/g*	*SH-level*[b] *mequivs/g*
1	1.030	0.094
2	1.030	0.091
3	0.980	0.085

[a] Hair reduced with 0.61 *N* thioglycolate, pH 9.2, for 30 min.
[b] Hair reduced with 0.30 *N* thioglycolate, pH 9.1, for 5 min.

during the longer treatment period, and for this reason an extraction time of two hours was chosen for thioglycolate removal.

Weight level study

The method developed was tested for reliability with different sample weights. Samples were prepared by immersion in 0.61 *N* ammonium thioglycolate solution for 20 min, followed by an isopropyl alcohol rinse and acetic acid extraction. Portions weighing from 10 to 40 mg were reacted with 10 mg iodoacetamide for 45 min, the pH was adjusted to 7.5, and an aliquot was titrated with 0.001 *N* silver nitrate solution. The results obtained are shown in Table IV. The data indicate that in the range between 4 and 15 μequivs, the results are not a function of the weight of sample taken.

TABLE IV

EFFECT OF SAMPLE WEIGHT ON THE RESULT FOR SULFHYDRYL LEVEL

Weight of hair mg	*SH-found microequiv.*	*SH-level mequivs/g*
10.0	3.86	0.772
20.1	7.86	0.782
30.1	11.71	0.760
40.1	15.40	0.768

Stability of sulfhydryl groups in reduced hair keratin

It was observed that the sulfhydryl level of a given hair sample would slowly decrease when it was allowed to remain in contact with the atmosphere for any appreciable length of time. Since meaningful results in an analysis could be obtained only if all of the mercaptan groups originally present in the sample were ultimately determined, it was mandatory that the sulfhydryl level be stabilized until the material was analyzed.

Storing the samples under nitrogen was found to be a convenient means for the stabilization. Samples from which all thioglycolate had been removed were merely placed in a desiccator, high purity dry nitrogen was flushed through the container for five minutes, and the desiccator was then closed. The results for two samples, over a period of 17 days, showed conclusively that samples stored under nitrogen maintain their original sulfhydryl content. These data are listed in Table V.

TABLE V

STABILITY OF HAIR KERATIN SULFHYDRYL WHEN STORED UNDER NITROGEN

Time of analysis after sample preparation, days	*SH-level[a] mequivs/g*	*SH-level[b] mequivs/g*
1	0.193	0.511
7	0.187	0.511
10	0.183	0.515
15	0.188	0.508
17	0.192	0.507

[a] Sample prepared by immersing hair in 0.30 *N* ammonium thioglycolate, pH 9.2, for 10 min.
[b] Sample prepared by immersing hair in 0.47 *N* ammonium thioglycolate, pH 9.1, for 15 min.

Recommended procedure

A detailed description of the method for the determination of the sulfhydryl content of reduced hair utilizing iodoacetamide is given below:

The sample is washed well with isopropyl alcohol and blotted dry. Approximately 75 mg of 1/8" lengths are placed into a small extraction thimble and treated with glacial acetic acid in a micro Soxhlet extraction apparatus for two hours, then the sample is rinsed with isopropyl alcohol and blotted dry. Approximately 20 mg of the material are placed in a tared test tube and dried for one hour at 110° in a vacuum oven. After the tube has cooled to room temperature in a nitrogen-filled desiccator, it is reweighed to ascertain the exact amount of hair which it contains. Between 9.8 and 10.2 mg of iodoacetamide and 10.0 ml of pH 10 buffer are added to the tube. The contents are stirred with a glass rod at 15-min intervals and, when 45 min have elapsed, a 5-ml aliquot is withdrawn by means of a pipette and transferred to a 50-ml beaker. Enough 6 *N* nitric acid is added to the beaker (usually 3 drops) so that the solution pH drops below 7, and then solid sodium bicarbonate is introduced until a new addition results in no visible carbon dioxide evolution; the pH of such a solution is between 7 and 8.

A silver electrode and one end of a 1 *M* ammonium nitrate – 4% agar salt bridge are placed into the beaker, the other end of the bridge being placed into another beaker containing 1 *M* ammonium nitrate solution and a Beckman fiber-type calomel electrode. The leads of the two electrodes are connected to a Beckman Model G pH meter, the lead from the silver electrode being placed into the upper receptacle.

Standard 10^{-3} *N* silver nitrate solution is delivered into the beaker from a 10-ml semimicro burette. Near the end-point, 0.060-ml increments are added; because of the drifting of the readings, approximately one minute is required to reach potential equilibrium near equivalence. The end-point of the titration is determined by a double-derivative method. The sulfhydryl level of the sample is calculated from the relationship:

$$\text{SH-level, mequivs/g} = \frac{N\ \text{AgNO}_3 \times \text{volume in ml} \times 2}{\text{Weight sample in g}}$$

A typical titration curve is shown in Fig. 1.

Estimate of standard error of method

An estimate of the standard error of the procedure was obtained by preparing a series of hair samples, ranging from very low to high sulfhydryl content, and analyzing duplicate samples. The desired levels of reduction were attained by immersing hair in various ammonium thioglycolate solutions, 0.26 *N* to 0.71 *N*, each adjusted to pH 9.0–9.2 with ammonia, for five, ten,and twenty minutes. The recommended method of analysis was followed.

The data obtained are shown in Table VI.

DISCUSSION

As was anticipated, the time required for the complete reaction between hair keratin sulfhydryl and iodoacetamide was substantially longer than the time needed to complete the reaction with soluble thiol compounds (two minutes)[14]. This fact, however, is not too surprising inasmuch as the iodoacetamide molecule must first diffuse into the interior of the hair fiber, and the iodide ion liberated must then diffuse from the hair fiber into the bulk of the solution before the reaction can be considered completed for the purposes of the analysis.

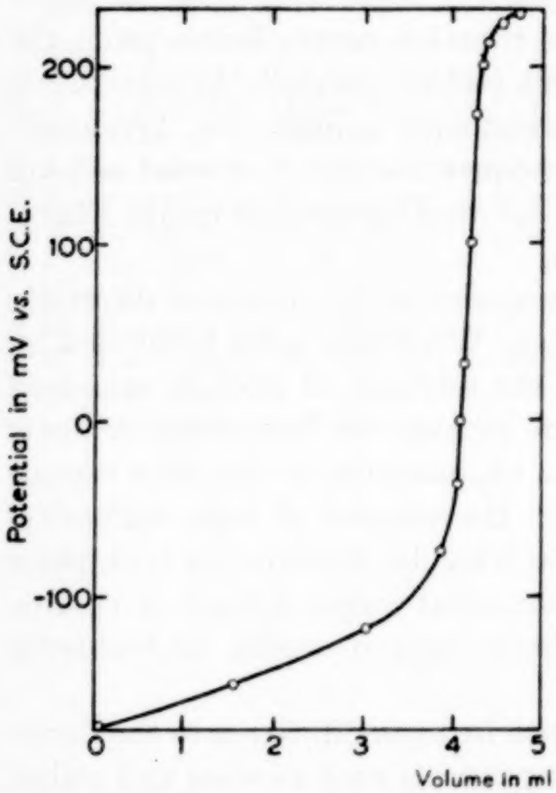

Fig. 1. Potentiometric titration of iodide ion with 10^{-3} N silver nitrate.

TABLE VI

DUPLICATE DETERMINATIONS OF THE SULFHYDRYL LEVEL OF HAIR REDUCED TO VARYING EXTENTS

Sample No.	*Sulfhydryl level, mequivs SH/g hair*	
1	0.001[a]	0.008[a]
2	0.083	0.082
3	0.097	0.105
4	0.120	0.122
5	0.167	0.160
6	0.201	0.207
7	0.224	0.216
8	0.227	0.223
9	0.311	0.312
10	0.320	0.336
11	0.346	0.351
12	0.399	0.400
13	0.411	0.408
14	0.503	0.506
15	0.509	0.548
16	0.637	0.644
17	0.783	0.778
18	0.850	0.831
19	0.840	0.876

[a] These values were obtained for an untreated hair sample.

It is apparent from the very low results obtained for the sulfhydryl content of the untreated sample, as reported in Table VI, that iodoacetamide reacts very slowly or not at all with side chains in the hair other than thiol groups. In addition to these particular results, other analyses of nonreduced hair were performed with this method and, in every case, a result below 0.010 mequivs SH/g hair was obtained. This fact is gratifying because the possibility of a side reaction with free amino groups exists[18] but apparently does not occur when the recommended procedure is followed.

The acetic acid extraction utilized for the removal of thioglycolate ion from the hair fibers proved to be satisfactory. However, a different system for the separation might be required if another reducing agent were employed. The exact conditions needed would be determined by the particular means of sulfhydryl group generation utilized; because of the success of the acetic acid extraction, it was not deemed necessary to examine other separation methods for the purposes of this investigation.

A regression analysis of the data in Table IV reveals that the estimate of the standard deviation of a single measurement is 0.074 μequiv. The value of "t" for the intercept is 1.00, so that there is insufficient evidence to maintain that the intercept differs from zero. In other words, there is no indication of a constant bias in the method.

The stabilization of the sulfhydryl level of a given hair sample was considered a prerequisite for the method since it is not always convenient to perform an analysis at the time the sulfhydryl groups are generated. The desired effect can be realized simply by storing the material in an inert atmosphere; samples kept in a nitrogen-filled desiccator in this laboratory were found to contain their original sulfhydryl content even after two months.

Some pH control of the iodide-containing solution being titrated with silver ion is necessary. If the pH is much above 8, hydroxide ion will begin competing for silver ion and will limit the "top" of the potentiometric titration curve. Below pH 7, the aerial oxidation of iodide ion becomes an important factor, especially in such dilute solutions. The means utilized in this work for pH adjustment, namely, the "breaking" of the pH 10 buffer with nitric acid and the subsequent addition of solid sodium bicarbonate until carbon dioxide evolution ceases, is a most convenient means whereby a suitable hydrogen ion concentration is assured.

The estimate of standard error of a single measurement in the 19 sets of duplicate results listed in Table VI is 0.010 mequivs SH/g hair. When this value is divided by the average result for mequiv. SH/g hair, 0.372, the estimate of average standard per cent error is found to be 2.7%. These values are perhaps not completely realistic because of the particular distribution of error. An examination of the data reveals that the largest discrepancies, by far, occurred in the samples of high sulfhydryl content. The major reason for this is probably that irregular reoxidation took place in these highly reduced samples, leading to a somewhat larger spread of results. Minimizing the sample's contact with atmospheric oxygen would undoubtedly decrease this source of variation.

The procedure developed should be applicable with little modification to the determination of sulfhydryl groups in other keratinous materials such as wool and callus. The simplicity and rapidity of the method and, especially, the fact that only those groups capable of reacting with iodoacetamide to produce iodide ions are determined, are particularly advantageous.

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SUMMARY

A method for the determination of the mercaptan groups in intact, that is, nonhydrolyzed, human hair has been developed. The procedure is based upon the titration with silver nitrate of the iodide ion generated in the reaction between the sulfhydryl groups in the hair and iodoacetamide. The standard error of the method is of the order of 0.010 mequivs mercaptan/g hair.

RÉSUMÉ

Une méthode est proposée pour le dosage des groupes mercaptans dans les cheveux. Ce procédé est basé sur le titrage, au moyen de nitrate d'argent, de l'ion iodure formé lors de la réaction entre les groupes sulfhydriles du cheveu et l'iodoacétamide.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung der Mercaptogruppen in Menschenhaar. Sie beruht auf der Reaktion der Sulfhydrylgruppen mit Jodoacetamid und Titration des gebildeten Jods.

Anal. Chim. Acta, 23 (1960) 89–97

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BUCHBESPRECHUNGEN

Ionenaustauscher, Band I, *Grundlagen. Struktur-Herstellung-Theorie*, von F. HELFFERICH, Verlag Chemie, G.m.b.H., Weinheim/Bergstr. 1959.

Wie so oft im Bereich der Chemie ist auch bei den Ionenaustauschern die Entwicklung der praktischen Anwendungen dem theoretischen Verständnis der ablaufenden Vorgänge weit voraus geeilt. Auch heute noch wird bei technischer, präparativer aber auch analytischer Anwendung der Ionenaustauscher überwiegend unter empirisch ermittelten Versuchsbedingungen gearbeitet. Wenn in den letzten Jahren vielfach theoretische Betrachtungen zum Thema "Ionenaustausch" angestellt worden sind, so sind diese doch unter derart verschiedenen Gesichtspunkten angesetzt worden, dass es demjenigen, der sich nicht speziell mit diesem Problem befaßt, schwer fällt, eine Übersicht zu erlangen zumal der Umfang des Stoffes groß ist. So wird vielleicht zu selten von den häufig recht nützlichen Ansätzen Gebrauch gemacht, die es gestatten, Manches über optimale Arbeitsbedingungen vorauszusagen oder näherungsweise zu berechnen, wenn bestimmte, das Material eines Ionenaustauschers charakterisierende Grössen bekannt sind oder gemessen werden. Es ist das besondere Verdienst des Autors, in dem hier vorgelegten Buch das weit verstreute, oft heterogene Material kritisch auswählend unter übergeordneten Gesichtspunkten zusammengefasst zu haben.

Entsprechend ihrer überragenden praktischen Bedeutung nimmt die Behandlung der Harz-Austauscher den bei weitem grössten Raum ein. Nach einleitenden Bemerkungen über Struktur und Wirkungsweise der Austauscher werden die verschiedenen Austauschertypen, auch anorganische und solche auf Kohle-Basis, nach Aufbau und Eigenschaften besprochen. Es folgen Kapitel über Herstellungsprinzipien und die Kapazität von Harz-Austauschern. Besonders ausführlich und den theoretisch interessierten Leser besonders ansprechend sind die Kapitel über Gleichgewichte und Kinetik an Ionenaustauschern, Probleme zu denen der Autor in eigenen Arbeiten Bemerkenswertes beigetragen hat sowie über elektrochemische Eigenschaften. In den Kapiteln Ionenaustauschermembranen und Ionenaustauscherpackungen wird der Praktiker auch unmittelbar nützliche Hinweise finden, z.B. Ansätze für die Berechnung von Säulenabmessungen und für die rechnerische Behandlung von Nichtgleichgewichtszuständen. Die abschliessenden Kapitel über das Verhalten von Austauschern in nicht wässrigen oder gemischten Lösungsmitteln, über Ionenaustauscher als Katalysatoren sowie Elektronen- und Redox-Ionen-Austauscher sind entsprechend ihrer spezielleren und meist geringeren Bedeutung kürzer gehalten aber doch mit einer für das Verständnis ausreichenden Ausführlichkeit behandelt worden. Mit dem mehr als 1000 Literaturzitaten, die dem Text beigegeben sind, dürften die wichtigeren Arbeiten bis etwa zum Jahre 1957 hin nahezu vollständig erfasst sein.

Niemand wird erwarten, dasz bei der Fülle des Materials auf alle möglichen Betrachtungsweisen eingegangen wurde. Der gröszte Teil der Leser wird eine einheitliche Darstellung der Grundlagen und der Theorie in einer Weise wünschen, wie sie nach heutiger Anschauung den tatsächlichen Verhältnissen am nächsten kommt. So hat der Verfasser unter Verzicht auf historisch interessante oder vielleicht aussichtsreiche aber schwer zu übersehende oder abstrakte Ansätze solchen Betrachtungsweisen den Vorzug gegeben, die eine sachlich begründete einheitliche Darstellung erlauben und bei guter Anschaulichkeit ein möglichst hohes Mass an Aussagen gestatten. Es ist ihm dabei ein Werk aus einem Guss gelungen, das dem Wunsch nach Anschaulichkeit, Exaktheit und Geschlossenheit der Darstellung in bemerkenswerter Weise Rechnung trägt. Ein flüssiger, durchsichtiger Stil und Prägnanz im Ausdruck machen das Buch leicht lesbar auch für Jemanden, für den Deutsch Fremdsprache ist. Hervorzuheben sind ferner die Konsequenz in der Anwendung von Symbolik und Nomenklatur, die klare Gliederung des Textes, die instruktiven, geschickt ausgewählten Zeichnungen sowie eine sehr gute drucktechnische Gestaltung und Ausstattung.

Das Buch wird, da es einem ausgesprochenen Bedürfnis entgegenkommt, von allen am Ionenaustausch Interessierten freudig begrüsst werden.

H. Bode (Hannover)

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Gmelins *Handbuch der anorganischen Chemie*, 8. Auflage, Verlag Chemie, G.m.b.H., Weinheim/Bergstr. *Magnetische Werkstoffe*, 2. Ergänzungsband zu Eisen, Teil D, 1959, xxxviii, 580 Seiten, 380 Fig., Kartoniert DM 321,—, Ganzleinen DM 326,—.

Dieser Ergänzungsband ist zugleich zugehörig zu den Systemnummern 52 (Chrom), 56 (Mangan), 57 (Nickel), und 58 (Kobalt). Nach einer Behandlung der Theorie des Ferromagnetismus (34 S.) erfolgt die Beschreibung der ferromagnetischen Elemente und Legierungen: Eisen (26 S.) und seine Legierungen (121 S.), Kobalt (11 S.) und Legierungen (13 S.), Nickel (63 S.) und Legierungen (42 S.), Legierungen des Mangans (22 S.), Legierungen des Chroms (2 S.), Ferromagnetische Halbleiter (121 S.). Sehr ausführlich behandelt sind neben den ferromagnetischen Elementen und den Systemen Fe-Co, Fe-Ni und Co-Ni vor allem das System Fe-Ni-Al und andere Systeme auf dieser Basis sowie das System Fe-Si. Bei den in den letzten Jahren besonders wichtig gewordenen Ferriten wurde die Literatur bis 1955 miterfasst. Auf Grund der technischen Bedeutung der magnetischen Werkstoffe wurde die Patentliteratur besonders beachtet und, nach sachlichen Gesichtspunkten geordnet, in einem besonderen Abschnitt „Patentschriften" (66 S.) angeführt. Wie alle neueren Gmelin-bände enthält auch dieser Band ein zweisprachiges Sachregister (deutsch und englisch) sowie Marginalien in englischer Sprache.

Der Inhalt dieses Sonderbandes steht auf gleich hohem Niveau wie die übrigen Gmelin-bände, obwohl er weniger den Chemiker als vor allem den Physiker und Ingenieur der Nachrichtentechnik interessieren wird.

K. Eder (Genf)

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Gmelins *Handbuch der anorganischen Chemie*, 8. Auflage, Verlag Chemie, G.m.b.H., Weinheim/Bergstr. *Cadmium* (Ergänzungsband), System Nr. 33, 1959, iv, xciv, 802 Seiten, 218 Fig., Kartoniert DM 508,—, Ganzleinen DM 513,—.

Dieser Ergänzungsband zu dem 1925 erschienenen Band Cadmium umfasst die Forschungsergebnisse der Periode 1924 bis Ende 1949, wobei jedoch bei der Behandlung des Cadmium–Nickel Akkumulators die Literatur bis etwa 1958 berücksichtigt wurde.

Die Einteilung folgt dem üblichen Schema: Vorkommen (19 S.), Darstellung (24 S.) und physikalische Eigenschaften (140 S.), elektrochemisches Verhalten (127 S.), chemisches Verhalten (21 S.) und physiologische Eigenschaften (3 S.), Legierungen (60 S.) und Verbindungen (300 S.). Besondere Beachtung wurde der technischen Gewinnung des Elementes sowie seiner Bedeutung im Cadmium–Nickel Akkumulator zuteil. Bei den Verbindungen wurden die Additions- und Komplexverbin-

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dungen mit anorganischen und organischen neutralen Liganden (Ammoniak, Aminen und aminartigen Verbindungen) ausführlich behandelt.

Der Ergänzungsband enthält ein deutsch-englisches Inhaltsverzeichnis sowie englische Marginalien im Textteil.

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Gmelins *Handbuch der anorganischen Chemie*, 8. Auflage, Verlag Chemie, G.m.b.H., Weinheim/Bergstr. *Silicium*, Teil B, (System Nr. 15): *Das Element und die anorganischen Verbindungen des Siliciums*. Deutsch-englisches Inhaltsverzeichnis und englische Marginalien im Textteil, 1959, iv, lix, 923 Seiten, 154 Fig., Kartoniert DM 570,—, Ganzleinen DM 575,—.

Dieser Band behandelt die Chemie und Physik des elementaren Siliciums sowie der anorganischen Si-Verbindungen: Hydride (Silane), Oxyde, Siloxane, Silanole, Siloxene, ferner die N-, Halogen-, Se-, Te-, B-, und C-Verbindungen des Siliciums.

Nach einer Beschreibung der verschiedenen Darstellungsmethoden im Laboratorium und in der Technik werden die physikalischen und chemischen Eigenschaften des Elementes behandelt, wobei besonders seine Eigenschaften als Halbleiter berücksichtigt wurden. Es folgt dann eine Zusammenstellung von spezifischen Nachweis- und Bestimmungsmethoden (*ca.* 100 S.) in den verschiedensten Materialien wie z.B. Metallen, Mineralien, Düngemittel, Farben und organischen Stoffen (Papier, Kohlen, Waschmittel, Drogen, Nahrungsmittel, usw.).

Unter den Verbindungen werden zunächst die Hydride (32 S.) und dann im grössten Teil des Bandes die Sauerstoffverbindungen (376 S.) behandelt. Während über das Monoxyd (11 S.) wenig Literatur vorliegt, ist sie über das Dioxyd und seinen Hydraten in deren verschiedenen Formen, Eigenschaften und Anwendungen umso umfangreicher. Im Anschluss an das Dioxyd werden die polymerisierbaren Siloxane, Silanole und Siloxene beschrieben.

Von den übrigen Siliciumverbindungen sind den Halogeniden, die teilweise als Ausgangsprodukte für die Herstellung der Silikone dienen, sowie dem Carbid, wegen seiner technischen Bedeutung, grössere Kapitel gewidmet.

Der Schluss des Bandes befasst sich mit der Glaselektrode (56 S.), deren Formen, Verhalten und Anwendungen.

Es braucht nicht hervorgehoben zu werden, dass auch dieser Band dem hohen Niveau entspricht, das dem Gmelin zuerkannt werden muss.

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Lehrgang für das anorganisch-chemische Praktikum von Prof. Dr. G. Schwarzenbach, Juris-Verlag, Zürich, 1959, 197 Seiten, 18 Abb., Kartoniert SFr 25,—.

Dieses kleine Werk ist vor allem als Einführung in das Chemiestudium gedacht und skizziert den Lehrgang, der sich an der ETH Zürich seit Jahren bewährt hat.

Die Gliederung des Stoffes ist so vorgenommen, dass dem Anfänger zunächst nützliche Ratschläge, die den Arbeitsplatz betreffen, gegeben werden, wozu auch eine Anleitung zum Glasblasen und Angaben über die verschiedenen Glassorten gehören. An Hand von kurz, aber präzis beschriebenen Versuchen wird der Anfänger dann mit den wichtigsten chemischen Operationen wie Filtration, Kristallisation, Destillation, usw. vertraut gemacht. Hierbei wird bereits auf die Vorteile der Arbeit mit kleinen Substanzmengen hingewiesen. Es folgen dann die Beschreibung der wichtigsten Elemente und deren Verbindungen an Hand typischer Vertreter. Die weiteren Kapitel behandeln Stöchiometrie, Reaktionsgleichungen, wässrige Lösungen, Protonenübertragung in wässriger Lösung, Metallkomplexbildung (inkl. Komplexometrie), Fällungsreaktionen und Redoxreaktionen. Der Schluss des Bandes (etwa 1/3) beschreibt die Nachweisreaktionen für Kationen und Anionen sowie Trennungsgänge.

Das Buch enthält viele praktische Hinweise, die auch dem erfahrenen Chemiker oft von grossem Nutzen sein können. Sehr zu begrüssen ist die knappe, aber dafür sehr präzise und klare Fassung des Textes der theoretischen Erklärungen und Versuche, wodurch es möglich wurde, ein grosses Stoffgebiet auf verhältnismässig wenig Seiten unterzubringen. Durch die einseitige Bedruckung (Photodruckverfahren) hat das Buch allerdings das Doppelte des notwendigen Umfanges erhalten. Seines Inhalts wegen kann der Lehrgang bestens empfohlen werden.

K. Eder (Genf)

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BOOK REVIEW

The Analysis of Titanium and its Alloys, 3rd Ed., Imperial Chemical Industries Ltd., The Kynoch Press, Birmingham 1959, Pp. 119. Price 21 s. (see also *Anal. Chim. Acta*, 22 (1960) 499.)

In the review reference is made to the procedure on page 85 of the publication, for the determination of phosphorus in samples of titanium 'containing more than 3% manganese'. The reviewer has incorrectly concluded that this statement contains a typographical error, and I wish to point out that the instruction as it appears in our publication is correct.

In the examination of titanium samples containing small amounts of manganese, oxidation of phosphorus to ortho phosphate is achieved by oxidation with permanganate. Samples containing relatively large amounts of manganese cannot be oxidised effectively in this way, because manganous salts catalyse the reduction of permanganate and hence oxidation of phosphorus is less efficient. For this reason, a manganous salt is added when samples already contain an appreciable amount of manganese, then permanganate is formed, as recommended in the procedure, by oxidation with potassium periodate. In this way, complete oxidation of phosphorus is achieved.

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ERRATUM

Anal. Chim. Acta, 21 (1959) 570, unter ERGEBNISSE: sind die Werte für 100 R_f folgendermassen zu verbessern:

Ba	38 - 44
Sr	54 - 60
Ca	64 - 72
Mg	81 - 85

THE DETERMINATION OF ^{235}U BY THE ISOTOPE DILUTION METHOD

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INTRODUCTION

One of the problems associated with the use of enriched uranium fuelled reactors is that of costing for the quantity of ^{235}U consumed, both by fission and by neutron capture, in the reactor. For some transactions a value may be calculated from reactor power levels, irradiation times etc., but where these factors are uncertain it is highly desirable that there should be available a method of assessing ^{235}U usage which is quite independent of the irradiation history of the fuel elements.

Methods involving the determination of the radioactivity of fission products are, to a greater or lesser extent, dependent upon a knowledge of irradiation conditions and "cooling" time, although in principle a method might be based on the determination of a stable fission product. Other methods could be envisaged for application to intact fuel elements but these would seem to offer formidable practical problems. However, as the quantity of ^{235}U originally present in a charge of fuel elements is clearly defined, and as the average usage may be of the order of 20%[1], one attractive approach would consist of a determination of the ^{235}U content of the irradiated fuel elements, thus giving the quantity consumed by difference. This would require a representative sample of the fuel elements and to obtain this by any method other than one involving their total dissolution would seem extremely difficult if not impossible. However this dissolution usually represents the first stage in a chemical processing plant, so an aliquot of plant feed solution could conveniently provide a sample suitable for a ^{235}U determination. This estimate could be based on a determination of total uranium combined either with an isotopic analysis or with corrections for production of ^{236}U and loss of ^{238}U, but the most fundamental approach would be a direct determination of the ^{235}U content and for this the isotope dilution method would seem the most suitable technique. This method involves the addition of a known quantity of tracer (in this case ^{233}U or natural uranium) to the sample, followed by chemical separation of the uranium and a mass spectrometric determination of the ^{235}U/^{233}U or ^{235}U/^{238}U isotope ratio. The quantity of ^{235}U may then be calculated from the quantity of tracer added and the appropriate isotope ratio, so the method does not require a quantitative recovery of the uranium.

Thus the purpose of the work described in this paper has been an attempt to find the precision of the isotope dilution method for the determination of ^{235}U in solutions which simulate diluted samples of the feed solution in a chemical plant designed to process enriched uranium–aluminium alloy reactor fuel. The published data for the Dounreay Chemical Plant have been used to define typical solution conditions[1].

The technique has already been applied to the determination of uranium in fuel element dissolver solutions at the Idaho chemical processing plant using a ^{233}U tracer[2,3]. In one paper the coefficient of variation for "cold" samples was reported as 0.22% for solutions of uranium concentration 5–20 g/l, and 1.1% for solutions in the range 0.5–3.2 g/l; for process samples the overall coefficient of variation was 2.7%[2]. In a later paper a series of standard deviations was quoted for a range of sample-spike ratios, and a minimum value of 0.56% obtained for a ratio of unity; in this case the overall value quoted for plant solutions was 1.85%[3]. Uranium was separated from the plant solutions by remote liquid–liquid extraction using 3% T.B.P./*n*-hexane, followed by a hydrogen peroxide precipitation[4]. Normally an aliquot of plant solution containing 1–2 mg uranium was taken, but occasionally the method was used for as little as 50–100 μg. A total of 50 μg of uranium (sample and tracer) was used for the mass spectrometric analysis.

The method has also been successfully used for the determination of natural uranium in sea-water using ^{235}U (93%) as the tracer[5]. In this case a total quantity of 0.6 μg of uranium was separated chemically and used for the mass spectrometric analysis, and the average coefficient of variation was approximately 0.5%.

Either natural uranium or ^{233}U could be used as the tracer for the required determination of ^{235}U. The former is readily available and has practically no associated health hazard, but its use involves additional mass spectrometry for it is necessary to determine the ^{238}U/^{235}U ratio for the plant solutions alone, as well as after the addition of the natural uranium tracer. The use of ^{233}U permits a direct determination of ^{235}U (for solutions which may be assumed to contain no ^{233}U) and so might be expected to yield slightly more precise results. In the interests of making a complete investigation both tracers were used in this work.

In any attempt to achieve high accuracy by the isotope dilution method it is necessary to ensure that no systematic errors are introduced by mass discrimination in the ion source or detector of the mass spectrometer. This may be achieved either by calibrating the mass spectrometer with mixtures of known quantities of ^{233}U and ^{235}U or of natural uranium and ^{235}U, or more simply by calibrating the tracer against a ^{235}U standard under the same conditions as those subsequently used for samples, and then using the tracer concentration determined in this way for the calculation of the ^{235}U content of the solutions under test. In either case any random error in the measurement must be included in the final assessment of the precision of the method. The second method was used in this work for it avoided the need for a gravimetrically standardised solution of ^{233}U.

It was considered that the final accuracy of the method should be at least better than 1%. Previous work has shown that 0.5% could be achieved fairly readily for the average standard deviation of a single value[5]. Thus for a calibration based on ten replicate analyses, and a determination of ^{235}U in a given solution based on six replicate analyses, the equivalent value of three times the overall standard error for the final mean value would be 0.8%. This should apply to a determination made using ^{233}U tracer. For one using natural uranium it was proposed to take two further aliquots from each solution to permit a determination of the ^{238}U/^{235}U ratio of the fuel element uranium, and this measurement would introduce an additional small uncertainty.

It is clearly desirable that if such a method is to be used on a routine basis for plant solutions the activity levels should be small enough to permit the addition of tracer to aliquots, and the separation of uranium for mass spectrometry to be made in a fume hood with little or no shielding. A typical feed solution in a chemical processing plant might be as follows: Al 2.5 M; Hg 0.02 M; ^{235}U 3.2 g/l; fission product activity 570 curies/l[1]. This corresponds to an activity level of ~ 180 μC/μg ^{235}U, so a portion of diluted feed solution sufficient for 6–8 determinations, each made with 2 μg ^{235}U, will contain only 2–3 mC of fission product activity. Also a set of six aliquots each containing 2 μg of ^{233}U represents a relatively safe quantity of α-activity to handle in a dry state in a well ventilated fume hood.

Thus a procedure may be envisaged in which an aliquot of feed solution (or a series of aliquots combined to be representative of a number of batches of fuel elements) is taken from a chemical separation plant, diluted in a cave, and a portion containing a few millicuries of β-γ activity removed for analysis. The following account describes an investigation of the precision which should be feasible for the determination of ^{235}U in such a solution. Four test solutions have been prepared, each containing uranium, aluminium and mercury in the appropriate proportions, and aliquots containing ~ 2 μg ^{235}U taken for replicate analyses. The investigation has been made on an essentially inactive basis, but the presence of fission products would be unlikely to have any significant effect for the concentration of any one of these is low with respect to uranium, and the chemical separation used is one which is known to remove the majority of fission products. It is worth stressing that the precision of the results reported later refers only to the analytical method. It includes no allowance for errors associated with taking a sample from a plant or with its dilution, or for errors which might arise from continuous operation of a plant as opposed to batch operation.

PREPARATION OF SOLUTIONS

a. ^{235}U standard

About 0.6 g of enriched ^{235}U oxide (93%) was weighed as U_3O_8 after being heated to a constant weight at 850° and 950°. An impurity analysis for the sample amounted to only ~ 0.02% of the uranium. The oxide was dissolved in nitric acid and diluted to a concentration of ~ 35 μg ^{235}U/g.

An aliquot of this solution was diluted to a concentration of ~ 2 μg/g, and this dilute solution used to calibrate the tracers; four more aliquots were used to prepare the solutions under investigation.

b. Solutions under investigation

In addition to the chemical composition of a plant feed solution it is necessary to consider the range of uranium isotopic compositions which might be encountered. The uranium supplied to a reactor of the Dounreay type contains, in the first instance, 93% ^{235}U[1]; it will be assumed that the rest is ^{238}U, although in fact there will probably be a small quantity of ^{234}U. In the reactor some 20% of the ^{235}U is consumed by fission, or by conversion to ^{236}U, and the resultant deficiency of ^{235}U may be made good in the chemical processing plant by the addition of more 93% ^{235}U. Thus as the fuel is cycled between the reactor and the chemical plant there will be a build up of the isotopes ^{234}U, ^{236}U, ^{237}U and ^{238}U[1]. However only changes in the ^{238}U/^{235}U ratio need be considered, for only these will affect determinations made using a natural uranium tracer. If losses of ^{238}U in the reactor are ignored, then in the course of seven cycles the ^{238}U/^{235}U ratio of the material returned to the plant will increase from ~ 0.09 to ~ 0.2.

Four solutions were prepared by mixing solutions containing ^{235}U (93%), natural uranium, aluminium nitrate, mercuric nitrate, and hydrochloric acid. Their approximate compositions were as follows:

Solution 1: ^{235}U (93%) 2 μg/g, natural uranium —, Al 40 μg/g, Hg 1 μg/g, HCl 5 *N*, ^{238}U/^{235}U ratio 0.06.

Solution 2: ^{235}U (93%) 2 μg/g, natural uranium 0.2 μg/g, Al 40 μg/g, Hg 1 μg/g, HCl 5 *N*, ^{238}U/^{235}U ratio 0.15.

Solution 3: ^{235}U (93%) 2 μg/g, natural uranium 0.5 μg/g, Al 40 μg/g, Hg 1 μg/g, HCl 5 *N*, ^{238}U/^{235}U ratio 0.3.

Solution 4: ^{235}U (93%) 2 μg/g, natural uranium 1.8 μg/g, Al 40 μg/g, Hg 1 μg/g, HCl 5 *N*, ^{238}U/^{235}U ratio 1.

Solutions 1, 2 and 3 were prepared to simulate the range of ^{238}U/^{235}U ratios which might arise during the recycling of fuel between the reactor and the chemical plant. Solution 4 was chosen in view of the possible extension of the method to less enriched material.

c. Tracers

^{233}U tracer. A solution of ^{233}U was prepared with a concentration of ~ 3 μg/g in 5 *N* hydrochloric acid. The sample had the following isotopic composition: ^{233}U 99.68%, ^{234}U 0.24%, ^{235}U 0.02%, ^{238}U 0.06%.

Natural uranium tracer. About 0.9 g of "Specpure" U_3O_8 was heated to constant weight at 850° and 950°, dissolved in nitric acid and diluted to a concentration of 120 μg/g. One aliquot was diluted to a concentration of ~ 4 μg/g; this dilute solution was calibrated against the ^{235}U standard, and used to determine the ^{235}U content of solutions 1, 2 and 3. A more concentrated solution (~ 20 μg/g) was used to determine the ^{235}U content of solution 4. These solutions were also made 5 *N* in hydrochloric acid. An impurity analysis for the same batch of "Specpure" U_3O_8 amounted to 0.04%.

ADDITION OF TRACERS

For each determination an aliquot of the tracer and of the sample was weighed into a polythene bottle.

a. Choice of mixing ratio

For a determination using ^{233}U as the tracer the most suitable ^{235}U/^{233}U ratio is unity, and in this series of determinations the values were included by the range 0.8–1.2.

For a determination made using natural uranium it is also necessary to measure the ^{238}U/^{235}U ratio for the sample before the addition of the tracer. If the ^{238}U/^{235}U ratio of the sample is R_S, and that of the mixture after the addition of tracer R_M, then errors in R_S will be effective in the difference $R_M - R_S$. To minimise uncertainties caused by any errors in the measurement of R_S, R_M was usually chosen to be approximately $10 \times R_S$; thus an error of 1% in R_S would cause one of only $\sim 0.1\%$ in $R_M - R_S$. Values of R_S and R_M are shown in Table I.

TABLE I

VALUES OF R_S AND R_M FOR ^{235}U STANDARD AND SOLUTIONS UNDER INVESTIGATION

Solution	R_s	R_M
^{235}U standard	0.06	1 – 1.5
solution 1	0.06	1.2 – 1.3
solution 2	0.15	1.7 – 1.8
solution 3	0.30	2.8 – 3.5
solution 4	0.97	6.4 – 10.2

b. Calibration of tracers

^{233}*U tracer:* 10 aliquots were mixed with aliquots of the ^{235}U standard.
^{238}*U tracer:* 10 aliquots were mixed with aliquots of the ^{235}U standard.
3 aliquots of the ^{235}U standard only were taken to permit a determination of its ^{238}U/^{235}U ratio.

The mixtures were evaporated to dryness in small beakers and transferred to mass spectrometer filaments as described below.

c. Determination of ^{235}U in solutions under investigation

From each of the four solutions the following aliquots were taken: 6 aliquots for the determination of ^{235}U with ^{233}U tracer, 6 aliquots for the determination of ^{235}U with natural uranium tracer, and 2 aliquots for the determination of the ^{238}U/^{235}U ratio for the sample.

CHEMICAL SEPARATION OF URANIUM

All solutions had been conditioned to be 5 *N* in hydrochloric acid, so a solvent extraction procedure using tri(iso-octyl)amine[6] could be applied directly to the mixtures of samples and tracers. Bromine water was added to the solutions to promote oxidation of uranium to the six valence state; this was not necessary for the present series of determinations, but it was done in order to ensure that this addition could cause no interference with the separation. However if the method were to be applied to solutions in which the uranium was not necessarily in the six valence state, it would be advisible to check the efficiency of this oxidation under the appropriate experimental conditions. The uranium was extracted with a 5% solution of tri(iso-octyl)amine in xylene and back-washed into water. The final solution was washed with xylene to minimise organic contaminants. The two phases were mixed by flushing them rapidly into and out of a blunt-ended spitzer for 30–50 seconds; the mixture was then separated in a centrifuge, and the required phase removed with a pointed spitzer.

The following procedure was used:

1. To the solution (1–3 ml) add 2 drops of bromine water and 1 ml of 5% (v/v) tri(iso-octyl)amine/xylene: mix, centrifuge, separate; 2. Repeat step 1; 3. Add 0.5 ml xylene: mix, centrifuge, separate; 4. To combined xylene fractions add 1 ml of water:

mix, centrifuge, separate; 5. Repeat step 4; 6. To combined water fractions add 1 ml of xylene: mix, centrifuge, separate; 7. Repeat step 6.

The procedure was checked using ^{233}U and ^{237}U as radioactive tracers, and also with a mixture of fission products obtained from an irradiated uranium-graphite pellet after ~ 150 days "cooling". The γ-spectrum showed the main components of this mixture to be zirconium, niobium, cerium and ruthenium. The separation of uranium was usually 90% or better, and the final solution contained 1–2% only of the fission product β,γ-activity.

The distribution of the γ-activity after the separation was determined in one experiment and found to be as follows:

original aqueous phase	96%;
washed tri(iso-octyl)amine-xylene extract	3%;
final aqueous solution	1%.

Usually two samples were treated together and the separation then required 20–30 minutes. Any one aliquot usually contained about 2 μg of ^{235}U, which in practice, for a solution from the Dounreay plant, would be associated with ~ 360 μC of fission product activity[1]. With the above procedure this should be reduced to ~ 15 μC in 10 min, and the final product should contain only ~ 5 μC of fission product activity.

PREPARATION OF SAMPLES FOR MASS SPECTROMETRY

The solutions of purified uranium were evaporated to dryness in small platinum dishes (fluorimeter trays) and organic matter destroyed by oxidation with nitric and perchloric acids. A little nitric acid was then added to the platinum dish, evaporated to small volume, transferred to a glass plate, and there evaporated to dryness; this process was repeated 2 or 3 times, and produced a deposit on the glass plate which was clearly visible, and which could easily be dissolved in a drop of water and transferred to a mass spectrometer filament. Subsequent experience with plutonium analyses has shown that a more concentrated deposit may be produced by using an indented microscope slide treated with "repelcote".

CONTAMINATION

Polythene and glassware were normally used once only; they were washed with nitric acid and rinsed thoroughly with water. The platinum dishes were fused first with sodium bisulphate and then with fusion mixture, and finally were immersed in boiling nitric acid. After the second fusion the dishes were checked in a fluorimeter and any indicating more than 0.002–0.004 μg uranium were recleaned. Gram quantities of uranium were not treated in the laboratory during the period in which this work was carried out, but otherwise no special precautions were taken to avoid atmospheric contamination.

A check on contamination by natural uranium was provided by measurements of the ^{238}U/^{235}U ratios for the aliquots to which ^{233}U tracer had been added. When the determination of the ^{235}U/^{233}U ratio had been completed a few measurements were made of the ^{238}U/^{235}U ratio. Atmospheric contamination would be indicated by variation of the ^{238}U/^{235}U ratio between aliquots from any one solution. The variation observed was not significant and would correspond to only 0.1–0.2% of the natural uranium added as tracer in the parallel series of determinations.

Contamination from reagents would show as a difference between the average ^{238}U/^{235}U ratio found for solution 1, and the value found directly by measurements with larger quantities (~ 25 μg) of the ^{235}U standard. Again the differences were barely significant and were equivalent to a contamination level of only 0.001 – 0.002 μg natural uranium.

MASS SPECTROMETRY

Isotopic analyses were made by the multi-filament technique using two Metropolitan-Vickers M.S.5 type mass spectrometers:

Determinations involving ^{233}U tracer were made with the prototype M.S.5.

Determinations with natural uranium tracer were made using a production instrument.

Neither could be said to be operating ideally so the results reported later represent values obtained under average working conditions.

a. Prototype instrument (^{233}U determinations)

Considerable difficulty was experienced with H.T. breakdown in the ion source. This was never explained satisfactorily and its main effect was to reduce the rate of analysis from a possible 3 samples per day to an average 2 samples per day. Little trouble was caused by background. The side filament carrying the sample was heated by a stabilised current.

b. Production instrument (natural uranium determinations)

No difficulty was caused by H.T. breakdown in the ion source, but for some samples the hydrocarbon background was troublesome. The current supply for the sample filament was not stabilised; also the Sorenson regulator was not working, but in our opinion this made little difference to the stability of ion beams, provided the mains voltage to the electronic units was maintained between certain fixed limits by means of a "Variac". The provision for scanning a spectrum was superior to the arrangement on the prototype instrument for it permitted a comparison of two isotopes to be made over shorter intervals of time.

c. General comments

Before they were used for the analysis of samples all filament units were cleaned in the mass spectrometer for 10–15 minutes, and then checked for contamination under normal operating conditions. Sources carrying samples were placed in the instrument and the filaments run at temperatures a little below the normal operating ones until the hydrocarbon background had fallen to an acceptable level. The samples were then analysed under such conditions that the contribution of ^{238}U from impurity in the filament material should be less than 2 mV. The most abundant isotope in the sample was usually recorded on the 5-V or 10-V ranges; occasionally for the ^{233}U determinations the 1-V or 2-V ranges were used. About 40 measurements of the isotope ratio were made for each sample.

EVALUATION OF RESULTS

Results were calculated using the following equations:

a. ***^{233}U determinations***

$$y = z(R'_M - R'_T) \times \frac{235}{233} \qquad (1)$$

where z = mass of ^{233}U added, y = mass of ^{235}U in the sample, R'_T = ^{235}U/^{233}U ratio for the ^{233}U tracer, R'_M = ^{235}U/^{233}U ratio for the mixture of sample and tracer.

b. Natural uranium determinations

$$y = w\,\frac{R_T - R_M}{R_M - R_S} \times \frac{1}{R_T} \times \frac{235}{238} \qquad (2)$$

where w = mass of ^{238}U added, y = mass of ^{235}U in the sample, R_T = ^{238}U/^{235}U ratio of natural uranium, R_S = ^{238}U/^{235}U ratio for the sample, R_M = ^{238}U/^{235}U ratio for the mixture of sample and tracer.

CALCULATION OF RANDOM ERRORS

For a set of measurements the standard deviation of a single value may be calculated as:

$$\sigma = \sqrt{\frac{\Sigma\,(\bar{x} - x)^2}{(n - 1)}}$$

The standard deviation of the mean value may be taken as the standard error:

$$\sigma_m = \frac{\sigma}{\sqrt{n}}$$

When 6 or 10 measurements have been made, the standard error has been taken to represent the uncertainty in the mean value; when only 2 or 3 measurements have been made the standard deviation has been used. The appropriate uncertainty (expressed as a percentage and denoted by *s.e.*) has been calculated for each function used in the calculation and an overall value found:

$$s.e._{\text{total}} = \sqrt{\Sigma\,(s.e.)^2}$$

The uncertainty finally quoted with each result is $3 \times s.e._{\text{total}}$.

a. ^{233}U determinations

The precision of the final result for a given solution involves two sources of error: the random error in the determination and that in the calibration of the tracer.

b. Natural uranium determinations

For a determination made using natural uranium as a tracer there are several more sources of random error, but most of these are small. The various sources of error are:

(1) Random error in the calibration of the natural uranium tracer. (2) Random error in the determination. (3) When the ^{238}U/^{235}U ratio used for a determination is somewhat different from unity (solutions 3 and 4), a range factor has to be used in the calculation of the isotope ratio R_M. If the percentage error introduced into the isotope ratio by the uncertainty in the range factor is $[s.e.(RF/R_M)]$, then the error in the final result is:

$$[s.e.(RF/R_M)] \times \frac{R_M}{R_M - R_S} \times \frac{R_T - R_S}{R_T - R_M}$$

(4) Errors also arise from the measurement of R_S, the ^{238}U/^{235}U ratio of the sample before addition of tracer. If the random error in the ratio is $[s.e.(R_S)]$ the uncertainty introduced into a determination is:

$$[s.e.(R_S)] \times \frac{R_S}{R_M - R_S}$$

(5) Similarly there is the effect of the error in the range factor (if required):

$$[s.e.(RF/R_S)] \times \frac{R_S}{R_M - R_S}$$

The errors described under (4) and (5) occur both in a determination and in the calibration of the tracer, but as the function $R_S/(R_M - R_S)$ usually has a value in the range 0.05–0.1, their effect is relatively small.

RESULTS

a. Calibration of tracers

The values in Tables II and III were calculated using equations (1) and (2), the measured isotope ratios, and the gravimetric value for the concentration of the ^{235}U standard. These measured tracer concentrations were then used with equations (1) and

TABLE II

^{233}U TRACER

Sample number	*$^{235}U/^{233}U$ ratio*	*Concentration of ^{233}U μg/g*	*Mean value*
29	1.131	3.195	
30	1.120	3.197	
31	1.013	3.197	
32	0.915	3.202	
33	0.965	3.192	3.200 μg/g
34	1.019	3.201	
35	1.131	3.201	Standard deviation of a single value = 0.16%
36	0.951	3.208	
37	0.980	3.202	Standard error of mean value = 0.05%
38	0.937	3.209	

TABLE III

NATURAL URANIUM TRACER

Sample number	*$^{238}U/^{235}U$ ratio*	*Concentration of ^{238}U μg/g*	*Mean value*
39	1.274	3.785	
40	1.274	3.785	
41	1.205	3.796	
42	1.319	3.799	
43	1.264	3.776	3.788 μg/g
44	1.265	3.791	
45	1.037	3.788	Standard deviation of a single value = 0.20%
46	1.465	3.794	
47	1.502	3.777	Standard error of mean value = 0.06%
48	1.259	3.789	
49	0.0639		
50	0.0636		
51	0.0636		

(2) to determine the ^{235}U content of solutions 1–4. (The above values are based on directly measured isotope ratios. If the conventional discrimination correction of $\sqrt{238/235}$ is applied to the results in Table III, the value found for the concentration of *total* natural uranium is 3.839 μg/g. This may be compared with the value 3.832 μg/g based on the mass of natural uranium oxide used to prepare the tracer solution).

b. Results for solutions under investigation (Tables IV, V and VI)

TABLE IV

RESULTS OBTAINED USING ^{233}U TRACER

Solution	*Sample number*	*$^{235}U/^{233}U$ ratio*	*Concentration of ^{235}U μg/g*	*Mean value*
Solution 1	1	0.936	1.925	
	2	0.961	1.940	
	3	0.931	1.924	1.935 μg/g
	4	0.946	1.931	
	5	0.978	1.935	Standard deviation of a single value = 0.57%
	6	1.031	1.954	
				Standard error of mean value = 0.23%
Solution 2	15	0.978	1.955	
	16	0.981	1.960	
	17	0.937	1.955	1.957 μg/g
	18	0.928	1.958	
	19	0.972	1.958	Standard deviation of a single value = 0.10%
	20	0.926	1.958	
				Standard error of mean value = 0.04%
Solution 3	52	0.980	1.947	
	53	1.053	1.947	
	54	0.969	1.953	1.951 μg/g
	55	0.900	1.959	
	56	0.982	1.948	Standard deviation of a single value = 0.24%
	57	1.020	1.949	
				Standard error of mean value = 0.10%
Solution 4	66	0.926	1.915	
	67	0.875	1.909	
	68	0.956	1.917	1.913 μg/g
	69	0.992	1.913	
	70	0.820	1.914	Standard deviation of a single value = 0.16%
	71	0.983	1.910	
				Standard error of mean value = 0.07%

TABLE V

RESULTS OBTAINED USING NATURAL URANIUM TRACER

Solution	*Sample number*	*$^{238}U/^{235}U$ ratio*	*Concentration of ^{235}U μg/g*	*Mean value*
Solution 1	7	1.233	1.945	
	8	1.301	1.939	
	9	1.160	1.939	1.939 μg/g
	10	1.241	1.945	
	11	1.195	1.932	Standard deviation of a single value = 0.31%
	12	1.197	1.931	
	13	0.0638		Standard error of mean value = 0.13%
	14	0.0653		

TABLE V (continued)

Solution	*Sample number*	*$^{238}U/^{235}U$ ratio*	*Concentration of ^{235}U µg/g*	*Mean value*
Solution 2	21	1.762	1.962	
	22	1.823	1.950	
	23	1.825	1.960	1.957 µg/g
	24	1.817	1.956	
	25	1.743	1.957	Standard deviation of a single value = 0.21%
	26	1.822	1.957	
	27	0.1536		Standard error of mean value = 0.08%
	28	0.1554		
Solution 3	58	3.405	1.946	
	59	3.210	1.984	
	60	3.491	1.955	1.961 µg/g
	61	3.103	1.966	
	62	3.364	1.962	Standard deviation of a single value = 0.67%
	63	2.809	1.956	
	64	0.2976		Standard error of mean value = 0.27%
	65	0.2972		
Solution 4	72	8.72	1.922	
	73	6.64	1.917	
	74	10.25	1.932	1.922 µg/g
	75	7.78	1.917	
	76	6.45	1.918	Standard deviation of a single value = 0.29%
	77	8.67	1.923	
	78	0.9682		Standard error of mean value = 0.12%
	79	0.9681		

TABLE VI

SUMMARY OF RESULTS FOR SOLUTIONS UNDER INVESTIGATION

	Concentration expected µg/g	*Concentration determined using ^{233}U tracer µg/g*	*Concentration determined using natural uranium tracer µg/g*
Solution 1			
value	1.932	1.935 ± 0.014	1.939 ± 0.010
$3 \times s.e._{\text{Total}}$		± 0.72%	± 0.51%
discrepancy		+ 0.16%	+ 0.35%
Solution 2			
value	1.957	1.957 ± 0.004	1.957 ± 0.008
$3 \times s.e._{\text{Total}}$		± 0.20%	± 0.39%
discrepancy		+ 0.03%	+ 0.01%
Solution 3			
value	1.948	1.951 ± 0.006	1.961 ± 0.017
$3 \times s.e._{\text{Total}}$		± 0.33%	± 0.85%
discrepancy		+ 0.12%	+ 0.68%
Solution 4			
value	1.913	1.913 ± 0.005	1.922 ± 0.008
$3 \times s.e._{\text{Total}}$		± 0.25%	± 0.42%
discrepancy		+ 0.03%	+ 0.47%

*** The uncertainty quoted with each result is 3 × total standard error. The discrepancies are based on the differences between values expressed to a further place of decimals.**

The mean values of the errors and discrepancies recorded in Table VI are as follows:

(*a*) for determinations made using ^{233}U tracer the mean value of 3× total standard error is 0.37%, and the mean value of the discrepancy is +0.09%;

(*b*) for determinations made using natural uranium tracer the mean value of 3× total standard error is 0.55%, and the mean discrepancy +0.38%.

DISCUSSION

a. ^{233}*U determinations*

For the determinations made using the ^{233}U tracer, the discrepancies between the values found and those expected are less than 0.2% and are not significant. The mean value of 3 × (total standard error) is equivalent to 0.37%, so if a value of 0.1% is assumed for errors in the preparation of the ^{235}U standard the overall accuracy of a determination based on six replicate analyses should be of the order of 0.5%.

The values found for the standard deviation of a single value are, for the four solutions, 0.57%, 0.10%, 0.24% and 0.16% respectively, giving a mean value of 0.27%. The standard error for the calibration of the tracer is equivalent to 0.05%, and making allowance for this the average standard deviation becomes 0.275%. If this value is used to assign limits to the "concentrations expected" listed in Table VI then of the twenty-four individual determinations made for the four solutions, twenty lie within the range $\pm 1\ \sigma$, three within the range $\pm 1\ \sigma$ to $\pm 2\ \sigma$, and for one determination (number 6) the random error is considerably greater than $2\ \sigma$. The distribution which might be expected theoretically is 16 : 7 : 1. Thus the mean overall value of 3 × standard deviation is 0.83%. If a value of 0.1% is again assumed for errors in the preparation of the ^{235}U standard, the overall accuracy ($3\ \sigma$) for a measurement based on a single determination should be of the order of 1%.

b. Natural uranium determinations

The determinations made using natural uranium as the tracer show some evidence of a small positive bias. The discrepancy may be attributed to random error for solution 1 (2 standard errors) but it is becoming significant for solution 3 (2.4 standard errors) and is quite significant for solution 4 (3.3 standard errors). It is possible that for solutions 3 and 4 systematic errors of the order of a few tenths of a per cent could have been caused by contributions from hydrocarbon background. This has not been established but much of the data is consistent with the suggestion.

The relative abundances of the various peaks of the background observed in a mass spectrometer may well vary from sample to sample, and also over the course of an isotopic analysis; in the absence of an exact relation all that can be stated is that the background peaks at mass numbers 233, 235 and 238 can be of comparable size (*e.g.* in one case 0.5 : 0.7 : 1), although this may not necessarily be true for every analysis. The effects of such a background should be negligible in the determination of a ^{238}U/^{235}U ratio of nearly unity; however as the ratio to be determined becomes increasingly different from one, it also becomes increasingly sensitive to background errors for the less abundant isotope is recorded using a more sensitive range of the amplifier. For the conditions under which the various ratios were measured the average errors introduced by a background of 1 mV at each of mass numbers 235 and 238 would be as follows: solution 1, solution 2, and calibration, ~0.02%

(^{238}U/^{235}U ratio 1.2–1.8; ^{235}U peak usually recorded on 5-V range); solution 3, ~0.07% (^{238}U/^{235}U ratio 3.0–3.5; ^{235}U peak usually recorded on 2-V range); solution 4, 0.1–0.2% (^{238}U/^{235}U ratio 6–10; ^{235}U peak recorded on 1-V or 2-V range). Thus only solutions 3 and 4 need be considered.

Before each isotopic analysis was made the sample was heated to a temperature just below the normal operating value and left until the background (monitored at mass numbers 230, 231, and 233) had fallen to an acceptable level. Ideally the background at mass number 233 should be at least less than 1 mV; however it was sometimes difficult to distinguish a background of 1 mV from the noise level of the amplifier, and it was also considered that if the investigation were to be of any real value it should proceed at an average rate of two mass spectrometric analyses per day. For solution 3 an examination of the mass spectrometer records shows that for five of the six determinations the peak at mass number 233 had fallen to 1–5 mV by the beginning of the isotopic analysis; similar sized peaks at mass numbers 235 and 238 would introduce an error of 0.1–0.3%. For sample 59 the peak at mass number 233 was much larger, falling from a value of ~ 40 mV at the beginning of the isotopic analysis to ~ 3 mV by the end of the analysis. For solution 4 special care was taken to minimise the effects of background and in this case, as the samples were so large (2 μg ^{235}U; 10–20 μg ^{238}U), it was possible to reduce the relative size of background peaks by decreasing the gain of the electron multiplier. An examination of the mass spectrometer charts shows that for analysis 75 the abundance of the peak at mass number 233 was less than 0.1 mV. For the remaining samples however the peak at mass number 233 may well have been 0.5–1 mV, but usually it could not be distinguished adequately from the noise level to permit identification or precise measurement.

While the data and the mass spectrometric records may be consistent with the introduction of small errors by hydrocarbon background, in the absence of a precise relation between the abundances of the various background peaks it would be difficult to prove that a bias had arisen in this way. However further support is given by the mass spectrometric analyses 64, 65, 78 and 79. These were the isotopic analyses

TABLE VII

RESULTS CALCULATED FROM ISOTOPIC ANALYSES 64, 65, 78 AND 79

Sample number	*^{238}U/^{235}U ratio*	*Concentration of ^{235}U μg/g*
Solution 3		
64	0.2976	1.938
65	0.2972	1.941
mean value		1.940 ± 0.012 μg/g
cf. concentration expected		1.948 μg/g
3 × *s.e.*$_{\text{Total}}$		± 0.63%
discrepancy		— 0.43%
Solution 4		
78	0.9682	1.912
79	0.9681	1.912
mean value		1.912 ± 0.004 μg/g
cf. concentration expected		1.913 μg/g
3 × *s.e.*$_{\text{Total}}$		± 0.20%
discrepancy		— 0.04%

for the uranium present in solutions 3 and 4, but as the preparation of these solutions involved the addition of known quantities of natural uranium the isotopic analyses may also be used to calculate the ^{235}U contents. These results are recorded in Table VII. If the background suggestion is accepted then for solution 3 if a positive bias is introduced into results based on the measurement of ^{238}U/^{235}U ratios of ~3, a negative bias might be expected for these ratios of ~0.3; for solution 4 the ^{238}U/^{235}U ratio is now ~1 instead of 6–10 so no bias would be expected.

The results obtained for the four solutions yield the following estimates of precision. The mean value of 3 × (total standard error) for a determination based on six replicate analyses and two isotopic analyses is 0.55%, and for a determination based on a single isotopic dilution determination combined with a single isotopic analysis the mean value of 3 × standard deviation is 1.2%. Thus the precision achieved by the method using natural uranium tracer is somewhat worse than that found using ^{233}U tracer, and in addition, for the analyses described in this paper, there is a mean bias of 0.4%.

CONCLUSIONS

The results obtained using ^{233}U as a tracer show an average precision ($3\,\sigma$) of 0.37% for a value based on six replicate analyses and 0.83% for one based on a single determination. No significant bias was observed. For the determinations made using a natural uranium tracer the corresponding mean values of the precision ($3\,\sigma$) are 0.55% and 1.2% respectively, and there is a mean bias of +0.4%. The inferior results obtained using the natural uranium tracer appear to be due to the following reasons:

(a) Additional measurements are involved, namely the determination of R_S, the ^{238}U/^{235}U ratio of the samples. In fact the uncertainty introduced by these measurements was relatively small. In the worst case (solution 2) its effect was to increase the overall standard error by a quarter, and for the four solutions the average value of 3 × (total standard error) was increased from 0.50% to 0.55%.

(b) Uncertainties are introduced when the ratio R_M is somewhat different from unity. The two ion beams are then measured on different sensitivity ranges so the uncertainty in a range factor calibration is introduced, and errors in the location of the base line become more important. It also seems probable that small errors may have been introduced by hydrocarbon background. If this contribution should vary from sample to sample then in addition to causing a small bias it would form a further source of random error.

(c) The current supply for the sample filament in the ion source was not stabilised.

A method based on the use of ^{233}U as a tracer would seem to be very suitable for the required determination of ^{235}U. The average measures of precision are given above, but an allowance must also be made for errors associated with the preparation of a ^{235}U standard (*e.g.* stoichiometry of the oxide, etc.) so a precision and accuracy of about 1% should be feasible for a single determination, and about 0.5% for a measurement based on six replicate analyses. In addition to this specific problem it is possible that the method could be used for other routine determinations of ^{235}U. Methods based on a determination of total uranium will also usually require an isotopic analysis of the uranium, and in view of the high isotopic purity of the ^{233}U tracer it is likely that this analysis could often be made satisfactorily in the presence of the tracer. Thus, where the precision of a single determination is adequate, the isotope dilution method could form an alternative or at least a supplementary method of analysis for relatively little further effort than that already required for the isotopic analysis.

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SUMMARY

This paper describes an examination of the precision which might be achieved by using an isotopic dilution method for the determination of ^{235}U in the feed solution of an enriched uranium fuel chemical processing plant such as the Dounreay M.T.R. chemical plant. Four solutions were prepared to simulate diluted samples of feed solution; they contained uranium with an isotopic content ranging from 93% ^{235}U to 50% ^{235}U. Separation of uranium was made by solvent extraction with tri(iso-octyl)amine, and isotopic analyses were then made using two Metropolitan-Vickers M.S.5 mass spectrometers. Both ^{233}U and natural uranium were examined as possible tracers. Using ^{233}U as the tracer the results for the four solutions yield a mean precision ($3\ \sigma$) of 0.37% for a result based on six replicate analyses, and 0.83% for one based on a single analysis. These values include the random errors involved in the mass spectrometric calibration of the tracer, but not errors associated with the gravimetric preparation of a ^{235}U standard, or those which would be concerned with taking a sample from a plant.

The results obtained using a natural uranium tracer are less satisfactory, and possible explanations are suggested.

RÉSUMÉ

Les auteurs ont effectué l'étude d'un dosage de l'uranium-235, par dilution isotopique. La séparation de l'uranium se fait par extraction dans un solvant. Les analyses isotopiques ont été faites au moyen de deux spectromètres de masse. En utilisant l'uranium-233 comme traceur, on arrive à une précision moyenne de 0.37%. Les résultats obtenus avec l'uranium naturel comme traceur sont moins satisfaisants.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Uran-235 nach dem Isotopenverdünnungsverfahren. Die Abtrennung des Urans erfolgt durch Extraktion mit einem organischen Lösungsmittel. Zur Isotopenanalyse werden zwei Massenspektrometer verwendet. Mit Uran-233 als Tracer erreicht man eine mittlere Genauigkeit von 0.37%. Natürliches Uran als Tracer ist weniger geeignet.

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STUDIES ON COORDINATION COMPOUNDS

XVIII. FORMATION CONSTANTS OF SOME METAL SALTS OF HYDROXYQUINONES

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INTRODUCTION

Several of the hydroxyquinones have important analytical applications. Most of these involve interactions with metal ions. Yet there have been almost no quantitative studies on the equilibria involved in these interactions. Hence, the present investigation was undertaken using the technique which was found to be useful in the case of the nitrosonaphthols[1]. Kojic acid, chlorokojic acid, and 3-hydroxyflavone were included for comparison.

EXPERIMENTAL*

Materials

5-Hydroxy-1,4-naphthoquinone (juglone) (Aldrich Chemical Co. Inc.) was recrystallized from ethyl alcohol: m.p. 152°; reported 153°[2]. 2-Hydroxy-1,4-naphthoquinone (lawsone) (Aldrich Chemical Co., Inc.) was recrystallized from ethyl alcohol: m.p. 189°(d); literature 190°[3]. 2-Hydroxy-3-methyl-1,4-naphthoquinone (phthiocol) was prepared from 2-methylnaphthoquinone by the method of FIESER[4]: m.p. 172°; reported 173°. 2-Hydroxy-3-(3′-methylcrotyl)-1,4-naphthoquinone (Aldrich Chemical Co., Inc.) was recrystallized from ethyl alcohol: m.p. 136°. 1-Hydroxy anthraquinone (Bios Laboratories, Inc.) was recrystallized from purified dioxane and dried at 110°: m.p. 190°; reported 192°[5]. 1,2-Dihydroxyanthraquinone (alizarin) (National Aniline Division) was recrystallized from absolute ethanol and dried at 115°: m.p. 289°; reported 290°[6]. 1,2-Dihydroxy-3-nitroanthraquinone (3-nitroalizarin) (Eastman Organic Chemicals) was recrystallized from purified dioxane and dried at 115°: m.p. 242°; reported 244°[7]. Sodium 3-alizarin sulfonate (Eastman Organic Chemicals) was a certified product and used as supplied. 1,3-Dihydroxyanthraquinone was prepared by Dr. H. D. KIVLIGHN: m.p. 264–265°; reported 262–263°[8]. 1,2,7-Trihydroxyanthraquinone (K & K Laboratories, Inc.) was recrystallized three times from dioxane. 1,8-Dihydroxyanthraquinone (chrysazin) (Eastman Organic Chemicals) was recrystallized from ethyl alcohol: m.p. 190°; reported 191°[9]. Kojic acid (Corn Products Refining Co.) was purified by sublimation: m.p. 154–156°; reported 154°[10]. Chlorokojic acid (Aldrich Chemical Co., Inc.) was recrystallized from water: m.p. 165°; reported 166°[11]. 3-Hydroxyflavone (Eastman Organic Chemicals) was recrystallized from ethanol: m.p. 171°; reported 170°[12].

1,8-Dihydroxyanthrone. Five grams of purified 1,8-dihydroxyanthraquinone in a 200-ml round bottom flask with a reflux condenser was mixed with 5 g of tin powder and 40 ml glacial acetic acid. The mixture was heated to boiling and, over a period of 8 h, 5 g conc. hydrochloric acid was added dropwise. The yellow precipitate was filtered, dried and recrystallized from ethanol: m.p. 178°; reported 178°[13].

1,8,10-Trihydroxyanthrone. Ten grams of 1,8-dihydroxyanthraquinone was dissolved in 250 ml warm chlorobenzene. To this was added the Raney nickel prepared by washing 20 g of the commercial catalyst with acetone followed by chlorobenzene. Hydrogen was started at 50 lb/in.^{2} and 27° and was complete in 3 h. The solution was warmed and filtered and the catalyst warmed with

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* All melting points are uncorrected.

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200 ml ethanol. The yellow crystals (2.6 g) which resulted upon combining and chilling the filtrates were recrystallized twice from Skellysolve C: m.p. 160–61°*.

Equilibrium measurements

All measurements were made in 75 vol % dioxane–water solutions at a constant temperature of 30.0° ± 0.1°. The apparatus, techniques and methods of calculation were those previously described[1] except for two differences. The solution of tetramethylammonium hydroxide used in titrations was made up in 75 vol % dioxane-water solution exactly like the solution being titrated. The calculations were extended to include the reliability in the average values on the basis of the 95% confidence interval[14,15]. The values of the dissociation constants are assembled in Table I and those for the formation constants in Table II. Both the low solubility and the weak acidity of several of the compounds under study caused difficulties.

TABLE I

VALUES FOR pK IN 75 VOL % DIOXANE–WATER SOLUTION AT 30°

	pK_1	pK_2
2-Hydroxy-1,4-naphthoquinone	8.05 ± 0.03	
2-Hydroxy-3-methyl-1,4-naphthoquinone	9.56 ± 0.03	
2-Hydroxy-3-(3′-methylcrotyl)-1,4-naphthoquinone	10.32 ± 0.05	
5-Hydroxy-1,4-naphthoquinone	13.29 ± 0.03	
1-Hydroxyanthraquinone	14.29 ± 0.02	
1,2-Dihydroxyanthraquinone	10.73 ± 0.03	
1,8-Dihydroxyanthraquinone	13.06 ± 0.02	
1,2-Dihydroxy-3-nitroanthraquinone	6.28 ± 0.05	14.08 ± 0.2
1,2,7-Trihydroxyanthraquinone	10.48 ± 0.04	
Kojic acid	12.29 ± 0.03	
Chlorokojic acid	12.02 ± 0.02	
3-Hydroxyflavone	13.98 ± 0.03	
Sodium 3-alizarin sulfonate (in water solution)	6.12	10.80

1,2,3-Trihydroxyanthraquinone was too insoluble in 75% dioxane for any measurements. On treating sodium 3-alizarin sulfonate with tetramethylammonium hydroxide a copious precipitate formed. Because of the dark red color which developed early in the titrations of the hydroxyquinones, the solutions which contained metal ions were filtered to make certain that the final system was homogeneous. No calculations were made for those systems which had even a small amount of precipitate. These included all of the metal ions in the cases of 1,2-dihydroxyanthraquinone and 1,2,7-trihydroxyanthraquinone. The anthrones were too weakly acid to permit measuring the pK's.

Infrared absorption spectra

All spectra were obtained with a Perkin-Elmer, model 21 recording infrared spectrophotometer, using sodium chloride optics. The spectra in the solid phase were made by incorporating the materials in potassium bromide pellets[16,17]. The frequencies of selected absorptions are given in Table III.

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* These directions were supplied by Dr. W. B. Wheatley of Bristol Laboratories Inc. who adapted them from K. ZAHN AND H. KOCH, *Ber.*, 71 (1938) 172.

TABLE II

VALUES FOR FORMATION CONSTANTS OF THE COMPLEXES OF HYDROXYQUINONES AND HYDROXY-γ-PYRONES WITH SEVERAL BIVALENT METAL IONS AT 30° IN 75 VOL% DIOXANE

	UO_2^{+2}	Cu^{+2}	Be^{+2}	Ni^{+2}	Co^{+2}	Zn^{+2}	Cd^{+2}	Mn^{+2}	UO_2^{+2}	Cu^{+2}	Be^{+2}	Ni^{+2}	Co^{+2}	Zn^{+2}	Cd^{+2}	Mn^{+2}
2-Hydroxy-1,4-naphthoquinone	7.27 ±0.02	6.77 ±0.05	5.62 ±0.13	5.59 ±0.03	5.71 ±0.03	6.14 ±0.02	5.35 ±0.04		6.07 ±0.02	5.68 ±0.02	4.62 ±0.02	5.29 ±0.06	5.07 ±0.06	5.41 ±0.02	4.88 ±0.02	
2-Hydroxy-3-methyl-1,4-naphthoquinone	8.39 ±0.03	7.73 ±0.07	ppt.	6.46 ±0.02		6.80 ±0.03			7.20 ±0.05	6.44 ±0.03]	ppt.	5.61 ±0.02		6.00 ±0.03		
2-Hydroxy-3-(3′-methylcrotyl)-1,4-naphthoquinone	8.73 ±0.05	8.18 ±0.04	ppt.	6.61 ±0.07	6.57 ±0.05	7.08 ±0.05			7.30 ±0.06	7.36 ±0.03	ppt.	5.86 ±0.04	5.54 ±0.05	6.08 ±0.07		
5-Hydroxy-1,4-naphthoquinone	11.84 ±0.05	11.24 ±0.05	ppt.	8.96 ±0.03	8.66 ±0.03	ppt.	ppt.	ppt.	10.53 ±0.08	9.67 ±0.04	ppt.	7.66 ±0.07	7.55 ±0.09	ppt.	ppt.	ppt.
1-Hydroxyanthraquinone	ppt.	12.04 ±0.04	12.01	9.47 ±0.03	ppt.	ppt.	ppt.	9.03 ±0.06	ppt.	10.83 ±0.04	11.44	8.74 ±0.06	ppt.	ppt.	ppt.	8.80 ±0.05
1,8-Dihydroxyanthraquinone	12.13 ±0.06	ppt.	ppt.	8.64 ±0.03	8.52 ±0.04	ppt.	ppt.	ppt.	11.03 ±0.04	ppt.	ppt.	7.92 ±0.07	7.86 ±0.07	ppt.	ppt.	ppt.
Kojic acid	—	—	10.07 ±0.06	9.72 ±0.03	9.46 ±0.03	10.38 ±0.03	9.81 ±0.03	9.81 ±0.03	10.23 ±0.02	10.13 ±0.02	7.81 ±0.05	7.57 ±0.04	7.49 ±0.02	8.58 ±0.03	7.43 ±0.06	7.47 ±0.06
Chlorokojic acid	—	ppt.	9.57 ±0.07	9.22 ±0.03	8.87 ±0.03	9.74 ±0.03	8.72 ±0.02	ppt.	9.93 ±0.03		8.63 ±0.05	7.42 ±0.06	7.14 ±0.07	8.01 ±0.05	7.32 ±0.03	ppt.
3-Hydroxyflavone	—	13.20 ±0.05		ppt.	9.91 ±0.04	11.03 ±0.06	9.70 ±0.02	ppt.		11.13 ±0.05		ppt.	ppt.	9.79 ±0.04	8.41 ±0.03	ppt.

TABLE III

SIGNIFICANT PEAKS IN THE INFRARED SPECTRA OF HYDROXYQUINONES AND HYDROXY-γ-PYRONES

	Solvent	*Hydroxyl*	*Carbonyl*		*C = C*
2-Hydroxy-1,4-naphthoquinone	KBr	3175br	1681s	1693s	1596s
2-Hydroxy-3-methyl-1,4-naphthoquinone	KBr	3340br	1662sh	1652s	1595s
	$CHBr_3$	3140br	1670s	1652s	1600s
2-Hydroxy-3-(3′-methylcrotyl)-1,4-naphthoquinone	KBr	3333s	1662s,sh	1643s	1595s
5-Hydroxy-1,4-naphthoquinone	KBr	3070br	1670s	1647s	1603s
1-Hydroxyanthraquinone	KBr	3077br	1672s	1639s	1593s
	$CHBr_3$	3020s			
1,2-Dihydroxyanthraquinone	KBr	3340br	1662s	1634s	1587s
1,3-Dihydroxyanthraquinone	KBr	3378br	1671sh	1638s	1595s
	CCl_4	2907			
3-Nitro-1,2-dihydroxyanthraquinone	KBr	3175br	1681s	1642s	1590s
	CCl_4	2951 2840	1681	1629	
1,8-Dihydroxyanthraquinone	KBr	3077br	1678s	1628	1603sh
1,2,7-Trihydroxyanthraquinone	KBr	3300br	1670s	1640sh	1595s
1,8-Dihydroxyanthrone	KBr	3000br 3330sh		1613s	1600s
1,8,10-Trihydroxyanthrone	KBr	2970br 3440sh		1634sh	1608s
Kojic acid	KBr	3175br		1664	1622s
Chlorokojic acid	KBr	3175br		1656	1632
3-Hydroxyflavone	KBr	3180		1630sh	1609s
	CCl_4	3320		1628	1550v.br

br = broad; s = sharp; sh = shoulder.

DISCUSSION

Dissociation constants

The values of the dissociation constants show a number of interesting points. Perhaps the most startling of these is the large difference ($\sim 10^5$) in the dissociation constants of juglone and lawsone. The difference probably is to be attributed largely to the difference in the strength of hydrogen bonding in a six-*vs.* a five-membered ring[18]. However, the fact that the carbonyl group is adjacent to the hydroxy group in lawsone and not in juglone also may be important. Substitution of alkyl groups in the lawsone molecule has the usual inductive effect of markedly reducing the acidity, apparently the more so, the larger the group. Further, the difference ($\sim 10^4$) in the dissociation constants of kojic acid and lawsone shows that a marked effect on the stability of the ring formed by hydrogen bonding may be produced by a change in the adjacent ring.

The acidity of 1-hydroxyanthraquinone ($pK = 14.29$) differs by only a factor of 10 from that of the corresponding naphthoquinone, lawsone. The effect of a fused benzo ring is much the same when values for kojic acid and 3-hydroxyflavone are compared. The nitro group in 3-nitroalizarin greatly increases the acidity of the proton of the adjacent OH group but has much less effect on the proton of the OH group adjacent to the carbonyl group (see below). The effect of the sulfonate group is similar since the pK's for alizarin in water at 18° are 8.18 and 11.94[19].

The substitution of $ClCH_2^-$ for $HOCH_2^-$ in kojic acid increases the acidity as would be expected but not by any great amount.

The pK's of such weak acids are best determined by some means other than simple titration. By measurements of the EMF of cells, KIVLIGHN[20] found the following values for 70% dioxane solution at 25°:

	pK_1	pK_2
1-Hydroxyanthraquinone	13.15	
2-Hydroxyanthraquinone	10.86	
1,2-Dihydroxyanthraquinone	9.93	16.37
1,4-Dihydroxyanthraquinone	12.23	13.92
1,5-Dihydroxyanthraquinone	12.66	15.23
1,8-Dihydroxyanthraquinone	11.89	15.15
2,6-Dihydroxyanthraquinone	10.32	12.75

While these values are different from those found in this investigation, the agreement is as good as might be expected considering the different conditions of the two sets of measurements. Some studies on the variation of pK with mole fraction of dioxane were made. In 70 volume % dioxane–water at 30° the following values were obtained: 1,2-dihydroxyanthraquinone, 9.91 and 1,8-dihydroxyanthraquinone, 11.97. KIVLIGHN's values show the difference in acidity of a hydrogen-bonded and a non-hydrogen-bonded OH group and indicate that both OH groups in 1,8-dihydroxyanthraquinone are hydrogen-bonded to the same carbonyl group. They also make evident why only pK_1 for these compounds can be determined titrametrically and why no pK at all for the reduction products of 1,8-dihydroxyanthraquinone can be obtained titrametrically.

Formation constants

For the compounds comprising the present study two customary generalizations hold: (1) for a related group of compounds and a common metal ion, the weaker the acid, the more stable the complex and (2) for a given chelating group, the order of stability of metal ion associations is $UO_2 > Cu > Zn > Be > Ni > Co > Mn, Cd$.

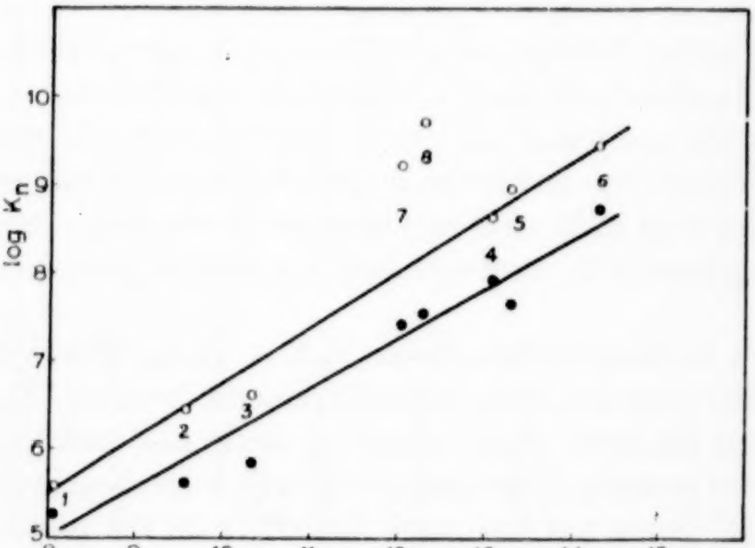

Fig. 1. Plot of log K_n for the nickel salts *vs.* pK of the ligand: o = log K_1; ● = log K_2; 1 = 2-hydroxy-1,4-naphthoquinone; 2 = 2-hydroxy-3-methyl-1,4-napthoquinone; 3 = 2-hydroxy-3(3'-methylcrotyl)-1,4-naphthoquinone; 4 = 1,8-dihydroxyanthraquinone; 5 = 5-hydroxy-1,4-naphthoquinone; 6 = 1-hydroxyanthraquinone; 7 = chlorokojic acid; 8 = kojic acid.

The beryllium compounds are thus relatively less stable than usual[21-23]. Insolubility of complexes prevented the determination of formation constants in several cases. The metal derivatives of lawsone are significantly more stable than those of juglone. It is not safe to conclude that, contrary to findings with other types of compounds [diamines and triamines[24,25] α- and β-(S-ethylmercapto)alkanoic acids[26], α- and β-aminopolyalkanoic acids[27,28]], six-membered chelate rings are here more stable than five-membered rings, because lawsone is a much weaker acid than juglone. The plot of pK *vs.* log K (Fig. 1) for the nickel derivatives indicates that the latter is the more likely explanation. Kojic acid differs too much in type from the hydroxyqui-

TABLE IV

SIGNIFICANT PEAKS IN THE INFRARED SPECTRA OF VARIOUS ANTHRAQUINONES

Compound	*Medium*	*Hydroxyl frequencies*		*Carbonyl frequencies*		*Ref.*
Anthraquinone	Mull			1676		30
	Mull			1675s		29,32
2-Methyl	Mull			1675		29
1-Hydroxy	Mull			1673	1636	30
	Mull			1667	1631s	29
	Mull		3058	1672	1635	32
2-Hydroxy	Mull	3509		1673		30
	Mull	3344s		1667s		29
1-Hydroxy-2-methyl	Mull			1696s	1634s	29
1-Hydroxy-2,4-dichloro	C_6Cl_6		2857			33
2-Hydroxy-3-methyl	Mull	3311s		1658s		29
2-Hydroxy-1-nitro	C_6Cl_6	3497sh				31
2-Hydroxy-3-nitro	C_6Cl_6		3185br			31
1,2-Dihydroxy	Mull	3380		1660	1636	30
	Mull	3367m		1658s	1634s	29
	C_6Cl_6	3320s	2967br			31
1,2-Dihydroxy-3-nitro	C_6Cl_6			1680	1640	31
1,3-Dihydroxy	Mull	3380		1675	1635	30
	Mull	3413s		1675m	1637s	29
	C_6Cl_6	3571s	3077br			31
1,4-Dihydroxy	Mull			1627		30
	Mull			1626		29
	Mull		2924	1626		32
1,5-Dihydroxy	Mull			1639		30
	Mull			1634		29
	Mull		2967	1636		32
1,8-Dihydroxy	Mull			1675	1622	30
	Mull			1678s	1621s	29
	C_6Cl_6		3101br			31
1,8-Dihydroxy-3-methyl	Mull			1675s	1621s	29
2,3-Dihydroxy	Mull	3472s	3268s	1675s		29
2,6-Dihydroxy	Mull	3300s		1656s		29
2,7-Dihydroxy	Mull		3195m	1653s		29
1,2,3-Trihydroxy	Mull	3378m		1650s	1626s	29
1,2,4-Trihydroxy	Mull	3226m			1621s	29
1,2,5-Trihydroxy	Mull	3333m			1626s	29
1,2,6-Trihydroxy	Mull	3356s	3279w	1650s		29
1,2,7-Trihydroxy	Mull	3390w	3310s	1647s		29
1,2,8-Trihydroxy	Mull	3378m		1661m	1621s	29
1,3,4-Trihydroxy	Mull	3330			1632	30
1,4,8-Trihydroxy	Mull				1605s	29
1,4,5,8-Tetrahydroxy	Mull				*ca.*1595	30
		3333			1590	32

nones for any rigorous comparison. However, the noticably greater value of log K_1 for the kojic and chlorokojic acid derivatives is interesting.

Infrared spectra

It was hoped that the infrared spectra as well as the dissociation constants of the hydroxyquinones would furnish information about the relative stability of hydrogen bonds in the compounds under study. This difference was expected to be manifest in the magnitude of the shifts of the hydroxyl and carbonyl absorptions from their normal positions. This expectation was not fully realized. Although the shifts seem to be of the relative magnitudes expected, other structural factors appear to have a much greater effect. The spectra of the anthraquinones have been rather thoroughly studied and data on pertinent compounds are assembled in Table IV. Certain generalizations have been drawn from these and other data[29].

1. Those compounds containing α, β-hydroxyl give a sharp band 3600–3150 cm^{-1}. 2. Those compounds containing an α-hydroxyl show a broad band at lower frequencies. Oftentimes this is completely obscured. 3. Those compounds having one α-hydroxyl show two carbonyl bands: one at 1675–1647 cm^{-1} and a stronger one between 1637 and 1621 cm^{-1}. 4. Those compounds having an α-hydroxyl at each carbonyl show one carbonyl band at 1645–1608 cm^{-1}. 5. Those compounds with two α-hydroxyls in the 1 and 8 positions show two carbonyl bands: one at 1678–1661 cm^{-1} and a stronger one at 1626–1616 cm^{-1}. 6. The average $C = C$ stretching frequency is greater than 1757 cm^{-1} in the 1,4- or 1,5-dihydroxy compounds and less than 1575 cm^{-1} in 1,4,5-trihydroxy. For the 1,4,5,8-tetrahydroxy compound, the $C = O$ and $C = C$ stretching frequencies are indistinguishable.

These observations on anthraquinone derivatives show clearly the effect of hydrogen chelation (hydrogen-bonding) in shifting the positions of the hydroxyl and carbonyl frequencies and in broadening the absorption bands, especially that for hydroxyl. The anthrones show the frequencies characteristic of a doubly hydrogen-bonded carbonyl and the hydrogen-bonded hydroxyl with the addition of the non-hydrogen-bonded hydroxyl in the case of 1,8,10-trihydroxyanthrone.

The absorption of the free carbonyl in juglone, which corresponds structurally to the anthraquinones, is in the same region as that of the anthraquinones (1672 cm^{-1}) although the hydrogen-bonded carbonyl is not shifted to as great an extent (1647 cm^{-1}) as in the anthraquinones. The absorption of the hydroxyl resembles that of the α-hydroxyanthraquinones. However, lawsone differs from juglone in that absorption due to the free carbonyl and the hydrogen bonded hydroxyl appear at higher frequencies (1681 cm^{-1} and 3175 cm^{-1}, respectively) whereas the absorption due to the hydrogen-bonded carbonyl in lawsone is at a lower frequency than in juglone. The expected difference due to the different strengths of the hydrogen bond in the two instances is not found. The marked influence of substitution in the 3-position of lawsone on the position of the free carbonyl absorption is surprising. The hydroxyl absorption of kojic and chlorokojic acids and 3-hydroxyflavone resembles that of lawsone whereas the carbonyl absorption resembles that of the 3-substituted lawsones. Also the absorption due to $C = C$ in these compounds is very close to that due to $C = O$.

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SUMMARY

Formation constants of various metal derivatives of four hydroxynaphthoquinones, two hydroxyanthraquinones, and three hydroxy-γ-pyrones have been measured in 75 vol% dioxane. The acidity of those of the above compounds which form 5-membered hydrogen chelate rings is greater than that of those which form similar 6-membered rings. The shifts of the hydroxy and carbonyl frequencies in the infrared spectra of these compounds are influenced by too many factors to be useful in distinguishing between the 5- and 6-membered rings.

RÉSUMÉ

Lors d'une étude sur les composés de coordination, les auteurs ont déterminé les constantes de formation de quelques dérivés métalliques d'hydroxyquinones (4 hydroxynaphthoquinones, 2 hydroxyanthraquinones et 3 hydroxy-γ-pyrones).

ZUSAMMENFASSUNG

Es werden die Bildungskonstanten verschiedener Metallderivate von vier Hydroxynaphtochinonen, zwei Hydroxyanthrachinonen und drei Hydroxy-γ-pyronen angegeben.

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PYROMELLITEIN INDICATORS

III. LAKE FORMATION

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The author has previously[1] discussed the pyromellitein indicators, prepared by condensing pyromellitic acid dianhydride (PMDA) with phenols by methods used for the preparation of phenolphthalein. Some of these indicators have been found to form colored lakes with metallic hydroxides.

Laboratory procedure

All of the experiments were run in semi-micro test tubes, by taking 1 drop samples of the ions, as made up for qualitative analysis, diluting to 1 ml, adding 1 drop of indicator, and observing any reaction which took place (Table II). If no precipitate formed, the solution was made basic with either 3 *N* NH_4OH (Table III) or 3 *N* NaOH (Table IV).

TABLE I

Indicator designation	*Phenol condensed*	*No. of phenols condensed per mole of PMDA*
A	Phenol	2
B	Phenol	4
C	Oxine	2
D	Oxine	4
E	Resorcinol	2
F	Resorcinol	4
G	Phenol	2
	Resorcinol	2
H	Brominated product of F	

TABLE II

COLORS OF PRECIPITATES FORMED IN WEAKLY ACID SOLUTION

Indicator	*Hg_2^{+2}*	*Pb^{+2}*	*Sb^{+3}*	*Sn^{+4}*	*Fe^{+3}*	*Fe^{+2}*	*Cr^{+3}*
D	—	—	—	—	—	Green	—
E	Yel.	Yel.	—	—	—	—	—
F	—	—	Yel.	—	(Red Br.)	—	—
G	Brn.	—	—	—	—	—	—
H	Red	—	Red	Orange	Red	—	Red

Note : Precipitates with Sb^{+3} and Sn^{+4} form on dilution. White precipitates formed by dilution are not listed. Pb^{+2} precipitates *very* small (haze).

TABLE III

COLORS OF LAKES FORMED IN SOLUTION BASIC WITH NH_3

Indicator	*Hg^{+2}*	*Bi^{+3}*	*Sb^{+2}*	*Sn^{+2}*	*Fe^{+3}*	*Al^{+3}*	*Cr^{+3}*
D	—	—	—	—	$Fe(OH)_3$	Grn.	$Cr(OH)_3$
E	Pink	Yel.	—	—	,,	—	,,
F	(Red Br.)	(Red Br.)	Yel.	Orange	,,	(Red Br.)	,,
G	Pink	Pink	—	—	,,	—	,,
H	Red	Bright Red	Red	Pink	,,	Red	Red

TABLE III (continued)

Indicator	*Co^{+2}*	*Ni^{+2}*	*Mn^{+2}*	*Fe^{+2}*	*Mg^{+2}*	*Be^{+2}*	*Ce^{+3}*
D	Grn.	—	Brn.[a]	(Gray Grn.)	—	—	Grn.
E	Gray	—	(Dk. Brn.)[b]	Grn.	Pink	—	Lt. Brn.
F	Orange	—	(Red Brn.)[b]	Brn.	Orange	Orange	Red Brn.
G	Gray	—	(Dk. Brn.)[b]	Grn.	Pink		Lt. Brn.
H	Red	Red	Red[b]	Dk. Red	Bright Red	—	Deep Red

[a] Possibly $MnO(OH)_2$.

[b] Indicator removed from solution; fluorescence destroyed.

TABLE IV

COLORS OF LAKES FORMED IN THE PRESENCE OF NaOH[a]

Indicator	*Hg^{+2}*	*Bi^{+3}*	*Cu^{+2}*	*Mg^{+2}*
E	Pink	Yel.	Grn.[b]	Pink
F	(Red Brn.)	(Red Brn.)	Yel. Grn.[b]	Orange
G	Pink	Pink	Grn.[b]	Pink
H	Red	Red	Purple	Bright Red

[a] Slight excesses of NaOH removed indicator from colored lakes in most cases. Those listed in Table III are those which seemed to be most stable.

[b] Colors of the copper lakes may be due to a suspension of colloidal $Cu(OH)_2$ suspended in the indicators.

The ions tested were grouped according to the classical scheme of analysis, as follows:

Ag^{+}, Hg_2^{+2}, Pb^{+2}, Hg^{+2}, Bi^{+3}, Cu^{+2}, Cd^{+2}, As^{+3}, Sb^{+3}, Sn^{+4}, Sn^{+2}, Fe^{+3}, Al^{+3}, Cr^{+3}, Ce^{+3}, Fe^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2}, Zn^{+2}, Be^{+2}, Ba^{+2}, Sr^{+2}, Ca^{+2}, Mg^{+2}

Of these ions some gave colors of such intensity that more experiments were run to determine the lower limits at which lakes were detected. These experiments were carried out by preparing solutions which were 200 p.p.m. with regard to the ion being used and dilution of this solution. Results are shown in Table V. If the lower limit is greater than 200 p.p.m., a line is shown in this table.

All indicators were prepared in concentrations of 0.100 g per 100 ml of solution, a drop of 0.1 N NaOH being added to aid solution. For purposes of tabulation, these

TABLE V

LOWEST ION CONCENTRATIONS (p.p.m.) GIVING DETECTABLE LAKES[a]

Indicator	Mg^{+2}	Ni^{+2}	Bi^{+3}	Sb^{+3}	Ce^{+3}	Cr^{+3}
E	50	50	—	—	100	—
F	12.5	25	—	—	100	200
G	12.5	50	—	—	100	—
H	1.5	25	100	100	50	100

[a] Lakes formed by making 1 ml of solution and 1 drop of indicator just basic with 1 *N* NH_3.

indicators will be designated by letters (Table I), according to the type of phenol and the number of phenolic groups condensed.

DISCUSSION

Indicators A, B, and C gave white precipitates or very weakly colored precipitates which have therefore been omitted in the tabulations. The very low indicator concentrations (amounting to the neighborhood of 0.1 millimole per l in the final mixture) producing intense colors seem to show the possibility of use of some of these in micro analysis. This is particularly true of the one designated as H, the brominated tetraresorcinol pyromellitein. The mercurous mercury compounds are destroyed by basic solutions, but might be used to determine mercurous mercury in the presence of silver and lead in solutions weakly acidified with dilute HNO_3. For qualitative testing, the use of indicator H for bismuth and for magnesium seems to have the greatest potential, since the indicator will show up the "water white" $Bi(OH)_3$, and since it gives an excellent stable color with magnesium but not with the other group IV metals.

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SUMMARY

The pyromellitein indicators previously described have been used to form lakes with a large number of ions. The brominated tetraresorcinol pyromellitein in particular forms brightly colored lakes with magnesium hydroxide which should be of interest in detecting this ion in very low concentrations.

RÉSUMÉ

Les indicateurs de la classe des pyromellitéines, décrits dans un article précédent, peuvent réagir avec un certain nombre de cations, en formant des laques. Un nouveau réactif très sensible est proposé pour l'identification du magnésium.

ZUSAMMENFASSUNG

Die in einer früheren Arbeit beschriebenen Pyromellitein Indikatoren bilden Farblacke mit einer grossen Anzahl von Jonen. Das bromierte Tetraresorcin-pyromellitein bildet mit Magnesiumhydroxyd einen stark gefärbten Lack, der als Nachweis für Magnesium dienen kann.

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HEMATOXYLIN AS INDICATOR IN THE CHELATOMETRIC TITRATION OF METALS

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Hematoxylin is obtained from Campeche wood and has been used as an indicator in the titration of aluminum with EDTA[1] and as a colorimetric reagent for aluminum[2] and other elements[3,4]. Hematoxylin itself does not give color reactions with metals; these are due to hematein, its oxidation product. In the present work the possibilities of using hematoxylin as an indicator in the titration of metals other than aluminum with EDTA are studied.

Reagents and apparatus

EDTA. A 0.025 *M* solution was prepared from 9.3 g of disodium ethylenediaminetetraacetate dihydrate diluted to one liter with water. It was standardized against zinc metal dissolved in dilute nitric acid, with Eriochrome Black T as indicator[5].

Standard bismuth solution. A 0.025 *M* solution was prepared from metallic bismuth (A.R.) by dissolution in nitric acid and dilution to one liter with 1 + 99 nitric acid. It was standardized with EDTA using Pyrocatechol Violet as indicator[6].

Standard zirconium solution. A 0.025 *M* solution was prepared from zirconyl chloride (A.R.) dissolved in hydrochloric acid (1 + 9). It was standardized with EDTA using Eriochrome Cyanine R as indicator[7].

Indicator. 0.2 g of hematoxylin (Merck, Germany) ($C_{16}H_{14}O_6 \cdot H_2O$) was dissolved in 1 ml of ammonia and 20 ml of distilled water; after 10 minutes it was acidified with 5 ml of acetic acid. This solution was stable for at least 3 months.

All the other reagents used were of A.R. quality.

The titrations were made with a Metrohm Piston Burette, Model E 274, 20-ml capacity.

The pH was measured with a Beckman Potentiometer, model Zeromatic, with glass and calomel electrodes.

Experimental procedure

A known volume of the standard metallic solution was transferred to a 250-ml beaker and diluted to about 150 ml with distilled water; the pH was adjusted with one or more of the following solutions: 1 + 99 nitric acid, 1 + 9 hydrochloric acid or 25% ammonium acetate. Ten drops of the indicator were added and the solution was titrated with EDTA, the burette tip being immersed and with the aid of magnetic stirring.

When necessary, the final pH was measured with the potentiometer.

Titration of bismuth

Excellent results were obtained for the determination of bismuth. The titration was successful at pH 1 to 2. If the pH was greater than 2, precipitation occurred and there was no color change on addition of EDTA. If the pH was less than 1 an orange-red color appeared, which made the end-point color change poor.

The color change of the indicator was from red to yellow and was very sharp and clear. Some typical results are given in Table I.

TABLE I

Bismuth present (mg)	*Bismuth found (mg)*	*Difference (mg)*
5.04	5.09	+0.05
10.08	10.14	+0.06
35.29	35.29	0.00
60.49	60.60	+0.11
100.82	100.83	+0.01

The titration was selective: lead, cadmium, zinc, aluminum, nickel, cobalt, calcium, barium, magnesium, silver and the alkali metals did not interfere. Small quantities of copper (about 30 mg) could be tolerated. Anions that precipitate bismuth, *e.g.* chloride, fluoride and phosphate, or that complex bismuth, *e.g.* tartrate and citrate, interfered. Reducing agents such as sulphite, bleached the indicator.

Iron(III) interfered, but its interference could be eliminated by the procedure described below.

Titration of bismuth in the presence of iron(III)

A few drops of 5% potassium thiocyanate were added to the acidic solution (pH 1–2) followed by a freshly prepared solution of 10% ascorbic acid, until discoloration was complete and 3 or 4 drops were present in excess. Then the indicator was added and the solution titrated immediately with EDTA.

TABLE II

TITRATION OF BISMUTH IN THE PRESENCE OF OTHER SUBSTANCES
(bismuth present: 50.41 mg)

Substance	*Amount*	*ml of EDTA required*	*Difference (ml)*
Na_2SO_4	1.0 g	9.42	+0.02
KNO_3	1.0 g	9.43	+0.03
NH_4NO_3	1.0 g	9.42	+0.02
$MgSO_4 \cdot 7\,H_2O$	0.2 g	9.40	0.00
$Ba(NO_3)_2$	0.2 g	9.40	0.00
$AgNO_3$	0.2 g	9.44	+0.04
$Co(NO_3)_2$	44.1 mg Co	9.44	+0.04
$NiSO_4$	44.1 mg Ni	9.46	+0.06
$Cu(NO_3)_2$	6.4 mg Cu	9.46	+0.06
$Cu(NO_3)_2$	31.8 mg Cu	9.45	+0.05
$Al(NO_3)_3$	27.0 mg Al	9.44	+0.04
$Al(NO_3)_3$	54.0 mg Al	9.40	0.00
$Ca(NO_3)_2$	0.10 g Ca	9.38	—0.02
$Zn(NO_3)_2$	0.10 g Zn	9.40	0.00
$Cd(NO_3)_2$	0.10 g Cd	9.40	0.00
$Pb(NO_3)_2$	0.10 g Pb	9.44	+0.04
$Fe(NO_3)_3$	30 mg Fe	9.44[a]	+0.04
$Fe(NO_3)_3$	50 mg Fe	9.43[a]	+0.03
$Fe(NO_3)_3$	100 mg Fe	9.36[a]	—0.04
$Fe(NO_3)_3$	100 mg Fe	9.45[a]	+0.05

[a] Fe(III) previously reduced with ascorbic acid.

The reverse titration of the EDTA with a solution of bismuth was possible. In this case the pH could be greater. This offers various possibilities for the determination of other metals by adding an excess of EDTA and back-titrating with a standard solution of bismuth.

TABLE III

TITRATION OF EDTA WITH A STANDARD SOLUTION OF BISMUTH

ml of 0.025 M Bi^{+3} solution		*Difference*	*pH at the end-point*
Calculated	*Found*		
10.64	10.70	+0.06	1.5
10.64	10.69	+0.05	2.3
10.64	10.71	+0.07	4.8

Titration of zirconium

In this case the color changed from red to pinkish-yellow but this was not very sharp; a very sharp color change was obtained by screening with 2 or 3 drops of 1% methylene blue. The color change was then from purple to greyish-green. The optimum pH was between 1.0 and 1.5.

TABLE IV

Zirconium present (mg)	*Zirconium found (mg)*	*Difference (mg)*
19.64	19.66	+0.02
19.64	19.68	+0.04
22.80	22.78	−0.02
22.80	22.82	+0.02
22.98	22.96	−0.02
22.98	22.92	−0.06
27.36	27.33	−0.03
34.20	34.15	−0.05
47.88	47.73	−0.15

TABLE V

TITRATION OF ZIRCONIUM IN THE PRESENCE OF OTHER SUBSTANCES
(zirconium present: 19.64 mg)

Substance	*Amount*	*ml of EDTA*	*Difference (ml)*
NaCl	1.0 g	8.81	−0.05
KBr	1.0 g	8.85	−0.01
KNO_3	1.0 g	8.83	−0.03
$MgCl_2 \cdot 6\,H_2O$	0.2 g	8.83	−0.03
$Al(NO_3)_3$	27 mg Al	8.89	+0.03
$Al(NO_3)_3$	54 mg Al	8.90	+0.04
$Ca(NO_3)_2$	100 mg Ca	8.79	−0.07
$Cd(NO_3)_2$	100 mg Cd	8.84	−0.02
$Co(NO_3)_2$	100 mg Co	8.83	−0.03
$Pb(NO_3)_2$	100 mg Pb	8.84	−0.02
$Zn(NO_3)_2$	100 mg Zn	8.86	0.00

The titration was less selective than that of bismuth. Copper was partially titrated even in small quantities. Iron, even in the presence of ascorbic acid, caused a poor color change. Anions that precipitate or complex zirconium, *e.g.* phosphates, fluoride or tartrate, interfered.

The reverse titration was not satisfactory because the color change was not sharp and it was easy to overshoot the equivalence point.

Titration of other metals

Lead reacted with hematoxylin at about pH 6 producing a blue color which changed to pink on addition of EDTA, but the results obtained were not satisfactory.

Copper reacted with hematoxylin to give a purple color; the color change on addition of EDTA depended on the pH and there was always a series of transition colors up to yellow (or green, for higher concentrations of copper). The results obtained were bad.

Several other metals, *e.g.* cadmium, cobalt, nickel, gave a violet or purple color with hematoxylin in alkaline media. With excess of EDTA this color changed to red but the contrast between the two colors was very poor.

SUMMARY

Hematoxylin is suggested as an indicator in the titration of several metals with EDTA. Bismuth and zirconium were readily determined in acidic medium. Several other metals also gave color reactions, but the color changes on addition of EDTA were not sharp.

RÉSUMÉ

L'auteur a étudié le comportement de l'hématoxiline, comme indicateur, lors du dosage de divers métaux, au moyen de l'EDTA. Les résultats obtenus lors du titrage du bismuth et du zirconium sont satisfaisants.

ZUSAMMENFASSUNG

Es wurde Hämatoxylin auf seine Eignung als Indikator bei der Titration von Metallen mit EDTA untersucht. Gute Werte werden bei der Titration von Bismut und Zirkonium erhalten.

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CHELATING AGENTS CONTAINING TWO 8-QUINOLINOL FUNCTIONS

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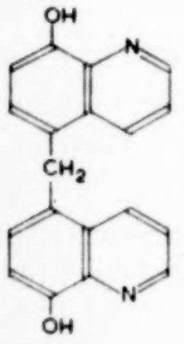
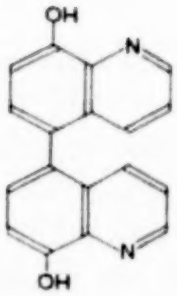
It has been stated that 8,8′-dihydroxy-5,5′-biquinolylmethane (I) and several closely related compounds are similar to 8-quinolinol in reactions with metals but are more sensitive[1]. Except for these observations there appears to be no other published information on the effects of more than one 8-quinolinol function per molecule on chelating properties.



I



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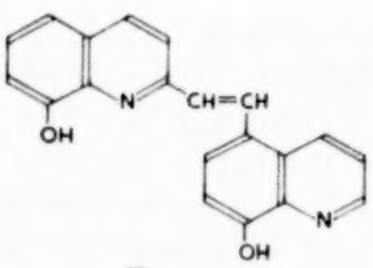

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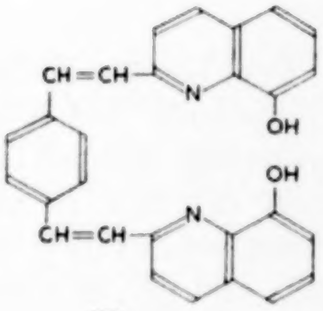

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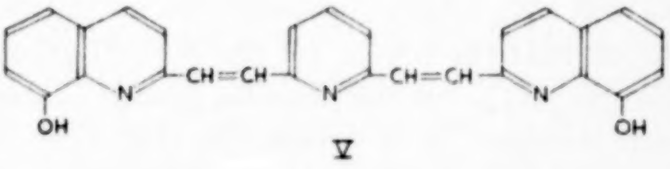

V

Five such reagents, three of them new compounds, were prepared for this study. Reaction of 8-quinolinol with formaldehyde in cold concentrated sulfuric acid[2] readily yielded I. Oxidation of 8-quinolinol with ferric sulfate[3] gave 8,8′-dihydroxy-5,5′-biquinolyl (II) but in very poor yields. Three new compounds were prepared by condensing 8-hydroxyquinaldine with 5-formyl-8-quinolinol[4], terephthaldialdehyde, and pyridine-2,6-dialdehyde respectively to give III, IV, and V. Of these III is the only one subjected to any investigation beyond the preparation at the present time. Both IV and V are extraordinarily insoluble in most solvents.

An attempt was made to evaluate the relative acid–base properties of I, II, and III by a spectrophotometric measurement of absorbancy as a function of pH (Fig. 1). The poor solubility of these reagents in water forced the comparison to be performed in 20% EtOH and even in this solvent at a concentration of only 4 mg per liter III precipitated at neutral pH values and thus was not investigated in the neutral to basic range.

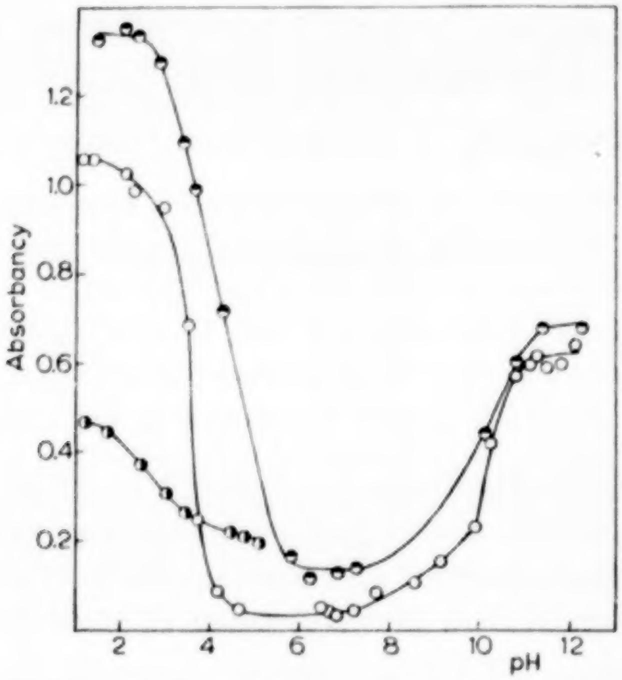

Fig. 1. Absorbancy *versus* pH curves: ◓ I at 258 mμ; ○ II at 258 mμ; ◑ III at 263 mμ.

Four possible ionization stages may be formulated for the dihydrochlorides of these compounds, and it was therefore rather surprising that only three spectrophotometrically distinct forms, representing only two ionization stages, were experimentally detected. In view of the nearly identical acid properties of the two N^+—H functions and their wide separation in the molecule it seems plausible to assume that pK_1 and pK_2 overlap to such an extent that they are not individually detectible. Thus the mid-point of the nearly vertical portions of the curves near pH 3–4 may be regarded as the average of pK_1 and pK_2. A similar argument may be applied to pK_3 and pK_4 which represent the ionizations of the two phenolic hydrogens. It is obvious that the $pK_{1av.}$ for the N^+—H groups is subject to much greater variation than the $pK_{2av.}$ for the phenolic groups (Table I); since the N^+—H dissociations are so much stronger, it is reasonable that they should exhibit greater vulnerability to structural factors. In any case, the presence of two 8-quinolinol functions per molecule gives a noticeable weakening of the base strength of the nitrogens but little change in the acidity of the phenolic groups.

TABLE I

APPARENT IONIZATION CONSTANTS OF 8-QUINOLINOLS IN 20% ALCOHOL

Compound	*Apparent* $pK_{1(av.)}$	*Apparent* $pK_{2(av.)}$
I	4.2	10.0
II	3.6	10.1
III	*ca.* 3.0[a]	—[a]
8-Quinolinol	4.9	10.3

[a] Accurate results for the first ionization of III were not obtainable because of precipitation, and for the same reason no effort was made to estimate the phenolic ionization.

Available comparative data for the ionization constants of other dihydroxy aromatic compounds are limited in number, but appear to give ratios of K_1 to K_2 generally much less than 100[5-7], except for hydroxyls ortho to each other or otherwise affected by specific steric interactions. Indeed for special cases, the ratio of K_1 to K_2 has been found to be less than the well-known statistical value of 4, and most remarkably, even less than unity[8].

TABLE II

ABSORPTION MAXIMA OF BIS-8-QUINOLINOLS IN 0.1 N ALCOHOLIC HYDROCHLORIC ACID

Compound			
I	257 (4.86)	311 (3.34)	380 (3.64)
II	257 (4.17)	311 (3.42), 320^a(3.39)	380 (3.64)
III	264 (4.65)	320 (4.23)	400–15 (4.45)
IV	264 (4.32)	325 (4.27)	420 (4.77)
V	300 (4.65)	360 (4.50)	386 (4.55)

Absorption maxima of all compounds in approximately 0.1 N alcoholic hydrochloric acid (Table II) were similar to the spectrum of 8-quinolinol in this solvent except for the shifts to longer wavelengths and higher absorbancies that might be expected from the extension of the conjugated system or the approximate doubling of the molecular weight.

A few chelates of compounds I, II and III were prepared and analyzed to establish whether both functions in these molecules can participate in chelation at once. Compound I formed chelates with both ferric and aluminum ions containing a 3:1 mole ratio of reagent to metal; thus, only one chelating function per molecule is used. Free hydroxyl groups could be demonstrated both by acetylation with acetic anhydride and pyridine and by infrared spectra. Similarly copper and zinc formed 2:1 compounds. Although II gave a 3:1 ratio of reagent to metal with aluminum, a 1:1 composition was noted with copper, nickel and zinc, indicating that both chelating functions in the molecule are used. A possible explanation for this effect might be formation of an oligomer with the metal acting as the connecting link between units, another possibility is simply incomplete chelation, the remaining valence bonds of the metal being used in reaction with hydroxyl or other ions that tend to produce an insoluble product. III forms a red-brown 2:1 chelate with cupric ion, and apparently only one chelating function per molecule is utilized.

In qualitative tests both I and II formed chelate compounds quite similar to those of 8-quinolinol in color and general pH response, and III resembled 8-hydroxyquinaldine in these respects.

EXPERIMENTAL

Preparation of compounds

The oxidation of 8-quinolinol with ferric sulfate to yield 8,8′-dihydroxy-5,5′-biquinolyl[3] was modified to give a yield of about 25%. Ferric sulfate (40 g) was added to 10 g 8-quinolinol in 2700 ml water with stirring, and the mixture heated 15–30 min. Then a solution of 15 g NaOH in 300 ml water was added at a rate to maintain the pH between 5 and 7 for 8–9 h at the boiling point. After standing over night the mixture was filtered and the black precipitate was warmed with a little concentrated hydrochloric acid until it became orange. After filtration the orange solid was dissolved in the minimum amount of water and concentrated hydrochloric acid added to precipitate the bright yellow dihydrochloride dihydrate. This could be washed with acetone, dissolved in water, and the solution neutralized to precipitate the white free base, decomposing above 310°. Bromination of the compound with standard bromate–bromide in an acid solution consumed four equivalents of bromine, indicating dibromination, probably in the 7,7′ positions. This bromination was quantitative and could be used to analyze the chelate compounds. Infrared spectra of the hydrochloride in KBr pellet form showed principal maxima at 3.03, 3.48, 6.14, 6.27, 6.43, 6.81, 7.21, 7.68, 8.35, 8.64, 9.28, 11.01, 11.75, 12.35 and 12.92 μ; the free base had principal bands at 2.99, 6.14, 6.30, 6.63, 6.80, 7.05, 7.15, 7.29, 7.82, 8.03, 8.31, 8.42, 8.67, 8.98, 9.64, 11.03, 11.86, 12.08, 12.28, 12.63 and 14.00 μ.

The preparation of I was readily accomplished by the method of SCHÜLLER[2]. The free base showed infrared maxima at 3.0, 6.15, 6.30, 6.64, 6.76, 7.03, 7.29, 7.83, 8.13, 8.36, 8.66, 9.30, 9.42, 10.04, 10.58, 11.01, 11.96, 12.10, 12.80 and 14.31 μ.

Compound III was obtained by heating 0.02 mole (3.2 g) 8-hydroxyquinaldine with 0.02 mole 5-formyl-8-quinolinol[4] in 10 ml acetic anhydride for 6 h. The resulting solution was poured into water, filtered and the precipitate saponified by heating for an hour with 20% sodium hydroxide solution. After neutralization of the solution with hydrochloric acid the precipitated product was filtered and recrystallized from alcohol containing 10% hydrochloric acid, yielding the dihydrochloride as orange crystals, melting at 233°. Principal infrared absorption bands for the dihydrochloride were observed at 3.6 (broad), 6.25, 6.43, 7.35, 7.60, 8.09, 8.62, 9.20, 11.45, 11.80, 12.19, 12.87 and 13.12 μ. Calcd. for $C_{20}H_{14}N_2O_2 \cdot 2HCl$: N, 7.20; found: N, 7.13.

A similar condensation of 8-hydroxyquinaldine with terephthaldialdehyde gave IV, as the dihydrochloride. Neutralization gave the free base m.p. 215°. Principal infrared bands were observed at 3.7 (broad), 6.24, 6.51, 6.62, 6.80, 7.00, 7.04, 7.20, 7.55, 7.70, 8.00, 8.27, 8.63, 9.19, 10.38, 11.52, 12.00, 13.40, and 14.72 μ. Calcd. for $C_{28}H_{20}N_2O_2 \cdot 2HCl$: N, 5.74; found: N, 5.63.

A similar reaction of two moles of 8-hydroxyquinaldine with 2,6-pyridine dialdehyde gave V as the trihydrochloride, m.p. 232°. Calcd. for $C_{27}H_{19}N_3O_2 \cdot 3HCl$: N, 8.00; found: N, 8.24.

Ionization constants and spectra

Stock solutions of I, II, and III containing 7.56, 4.90 and 4.30 mg per liter respectively in dilute hydrochloric acid were prepared. Portions (5.00 ml) of each were pipetted into 25-ml flasks, 5 ml ethanol added, and the solutions diluted with hydrochloric acid or dilute sodium hydroxide to 25.00 ml. An ionic strength of approximately 0.1 was provided by the addition of the necessary amount of potassium chloride to each before dilution. The apparent pH of the solutions was measured with a Beckman Model G pH meter calibrated against aqueous buffers. The spectra were recorded from 356–220 mμ with a Beckman DK-2 Spectrophotometer; a few of the solutions were also measured throughout the visible spectrum as well.

Separate alcoholic acid solutions were employed to obtain the spectra of Table II.

Infrared spectra were determined in KBr pellets on a Baird AB-2 Spectrophotometer with NaCl prism from 2–16 μ.

Chelate compounds

Since the formulas of the metal chelates were the principal point of interest, some preparations were conducted with both 2:1 and 1:1 ratios of reagent to metal ion when the ion was divalent, and with both 3:1 and 3:2 ratios for the trivalent ions. With I and ferric ion only a black 3:1 product was isolated and the same ratio was found for the yellow aluminum chelate; the presence of free hydroxyl groups in the latter was shown both by acetylation with acetic anhydride in pyridine and by absorption in the 3.0-μ region of the infrared spectrum. With the divalent ions copper and zinc, I formed only the 2:1 chelates. Reaction of III with copper also gave a red-brown 2:1 product. Reaction of II with aluminum gave the 3:1 product expected, but with copper, nickel and zinc this reagent yielded chelates analyzing for the 1:1 mole ratio.

All products were precipitated under the conditions normally employed for the preparation of the corresponding chelates of 8-quinolinol[9], and the dried samples were analyzed by ignition of weighed portions to the metal oxides. With II some analyses were also performed by bromination.

ACKNOWLEDGEMENT

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SUMMARY

Ionization constants, spectra and some metal chelate formulas of several chelating agents containing two 8-quinolinol functions per molecule have been investigated. In general, only one of the chelating functions appears to be used in the formation of insoluble metal chelates. However, 8,8′-dihydroxy-5,5′-biquinolyl may show exceptions to this rule with some divalent ions.

RÉSUMÉ

Les auteurs ont effectué une étude sur plusieurs agents de chélation, renfermant deux radicaux d'hydroxy-8-quinoléine par molécule. Ils ont examiné les constantes d'ionisation, les spectres et les formules de quelques chélates métalliques.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über chelatbildende Verbindungen, die zwei 8-Oxychinolingruppen pro Molekül enthalten. Ionisationskonstanten, Spektren und Strukturen einiger Metallchelate wurden bestimmt.

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DETERMINATION OF SMALL AMOUNTS OF CHLORIDE BY VOLHARD TITRATION*

EVALUATION OF OPERATOR DETERMINATE END-POINT ERROR

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The applicability of the Volhard titration to the determination of small amounts of chloride[1] in solid-rocket oxidants (ammonium nitrate, ammonium perchlorate, and potassium perchlorate) has not been ascertained prior to this time. In the course of determining the optimum experimental parameters of the Volhard titration, the recognition and empirical evaluation of the operator determinate end-point error was required. The determination and use of this value, or use of a procedure which eliminates the need of its evaluation, is required when one titrates in solutions of high ionic strength, and is applicable to all analyses involving back-titrations and visual end-point detection.

The original Volhard[2] titration of silver has been utilized for the determination of chloride in acid solution. An excess of silver ion is added (1), and the excess is titrated with thiocyanate ion (2), in the presence of ferric ions, which serve as an internal indicator through formation of the familiar dark red coloration of the iron(III) monothiocyanate ion. In order to prevent metathesis of the silver chloride to silver thiocyanate (3) which occurs in the vicinity of the end-point[3,4], nitrobenzene is added as coagulating agent[5]. After the equivalence point has been reached, a slight excess of thiocyanate ion is required to develop sufficient ferric thiocyanate ion to permit visual perception (4):

$$Ag^+ + Cl^- \rightarrow AgCl_{(s)} \tag{1}$$

$$Ag^+ + CNS^- \rightarrow AgCNS_{(s)} \tag{2}$$

$$AgCl + CNS^- \rightarrow AgCNS + Cl^- \tag{3}$$

$$Fe^{+3} + CNS^- \rightarrow Fe\,CNS^{+2} \tag{4}$$

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The absolute magnitude of the concentration of $FeCNS^{+2}$ at the end-point will depend upon the sensitivity of the operator's eye and the ionic equilibria established by the conditions of the titration. The error introduced because of these parameters is determinate and varies between operators, henceforth this error shall be called the operator determinate end-point error. Because thermodynamic equilibria data is available, or can be estimated, for all the ionic species involved in the titration, it is possible to calculate the total determinate error incurred at the end-point of the Volhard titration. However, in the estimation of small quantities of chloride with the aid of the Volhard titration, the operator determinate end-point error is large with respect to theoretical errors resulting from over titration at the end-point. Consequently, an expedient to alleviate the calculation of the thermodynamic concentration of species in the solution is to empirically evaluate the operator determinate end-point error and appraise the merits of the titration after suitable correction for this error. The empirical evaluation is a superior approach because of limitations of adequate mathematical expressions for the diverse ion effects at the high ionic strengths encountered. A rigorous discussion of the operator determinate end-point error, $F[(FeCNS^{+2})_i, \mu]$, the free chloride in solution, Cl^-, and their dependence upon the visual perception of the operator, $(FeCNS^{+2})_i$, and the ionic strength, μ, is given below.

Significance of the operator determinate end-point error

Equations 1, 2, and 4 may be written in terms of the thermodynamic relationships (5), (6) and (7).

$$(Ag^+)\,(Cl^-) = \frac{K_{AgCl}}{\gamma_{Ag^+}\,\gamma_{Cl^-}} \tag{5}$$

$$(Ag^+)\,(CNS^-) = \frac{K_{AgCNS}}{\gamma_{Ag^+}\,\gamma_{CNS^-}} \tag{6}$$

$$\frac{(FeCNS^{+2})}{(Fe^{+3})\,(CNS^-)} = K_f\,\frac{\gamma_{Fe^{+3}}\,\gamma_{CNS^-}}{\gamma_{FeCNS^{+2}}} \tag{7}$$

where K and γ are activity products and activity coefficients of the product or species denoted by the subscript; K_f is the activity formation constant of the ferric monothiocyanate ion.

The excess of ferric ion is sufficient that the analytical concentration and equilibrium concentration are approximately equal; *i.e.*,

$$(Fe^{+3})_0 = Fe^{+3} + FeCNS^{+2} \simeq Fe^{+3} \tag{8}$$

when this condition is satisfied, eqn. (7) is equivalent to

$$\frac{(FeCNS^{+2})_i}{(Fe^{+3})_0\,(CNS^-)} = K_f\,\frac{\gamma_{Fe^{+3}}\,\gamma_{CNS^-}}{\gamma_{FeCNS^{+2}}} \tag{9}$$

where $(FeCNS^{+2})_i$ is the concentration of ferric monothiocyanate ion required to be visually perceptible by the operator, and the ions with subscript o represent the analytical concentration of such ions. At the end-point of the titration, the total number of millimoles of chloride, silver, and thiocyanate present in the mixture are given by eqns. (10), (11) and (12):

$$(Cl^-)_0 = (Cl^-) + AgCl_{(s)} \tag{10}$$

$$(Ag^+)_0 = (Ag^+) + AgCl_{(s)} + AgCNS_{(s)} \tag{11}$$

$$(CNS^-)_0 = (CNS^-) + AgCNS_{(s)} + (FeCNS^{+2})_t \tag{12}$$

combining eqns. (10), (11) and (12).

$$(Cl^-)_0 = (Ag^+)_0 - (CNS^-)_0 + (FeCNS^{+2})_t + (CNS^-) - (Ag^+) + (Cl^-) \tag{13}$$

By incorporation of eqns. (5), (6) and (9), eqn. (13) becomes

$$\begin{aligned}(Cl^-)_0 = (Ag^+)_0 - (CNS^-)_0 + (FeCNS^{+3})_t + \frac{(FeCNS^{+2})_t\, \gamma_{FeCNS^{+2}}}{(Fe^{+3})_0 K_f\, \gamma_{Fe^{+3}}\, \gamma_{CNS^-}} \\ - \frac{(Fe^{+3})_0\, K_{AgCNS}\, K_f\, \gamma_{Fe^{+3}}}{(FeCNS^{+2})_t\, Ag^+\, \gamma_{FeCNS^{+2}}} + \frac{(FeCNS^{+2})\, K_{AgCl}\, \gamma_{FeCNS^{+2}}}{(Fe^{+3})_0\, K_{AgCNS}\, K_f\, \gamma_{Fe^{+3}}\, \gamma_{Cl^-}}\end{aligned} \tag{14}$$

or, the number of millimoles of chloride present in the sample is

$$(Cl^-)_0 = (N_{AgNO_3})\,(V_{AgNO_3}) - (N_{KCNS})\,(V_{KCNS}) + F[(FeCNS^{+2})_t, \mu] + (Cl^-)\,[(FeCNS^{+2})_t, \mu] \tag{15}$$

where N is the normality and V is the volume in milliliters of the solution noted by the subscript, $(Cl^-)[FeCNS^{+2})_t, \mu]$ indicates that the free chloride concentration is a function of $(FeCNS^{+2})_t$ and the activity coefficients, hence the ionic strength, μ, and

$$F[(FeCNS^{+2})_t, \mu] = (FeCNS^{+2})_t + (CNS^-) - (Ag^+) \tag{16}$$

The term $F[(FeCNS^{+2})_t, \mu]$ is defined as the operator determinate end-point error.

Evaluation of the operator determinate end-point error

In a manner analogous to the preceeding discussion, for the standardization or titration of a blank, eqn. 15 may be reduced to

$$N_{KCNS} = \frac{(N_{AgNO_3})\,(V_{AgNO_3}) + F[(FeCNS^{+2})_t, \mu]}{V_{KCNS}} \tag{17}$$

Hence, if $F[(FeCNS^{+2})_t, \mu]$ is significant with respect to $(N_{AgNO_3})\,(V_{AgNO_3})$, the normality calculated for potassium thiocyanate is not independent of the ratio V_{AgNO_3}/V_{KCNS}. However, if the ratio is (1) determined at the same ionic strength (constant activity-coefficient ratios), (2) by the same operator [constant $(FeCNS^{+2})_t$], and (3) exactly the same volume of potassium thiocyanate used in the standardization (17) is required for the back titration of the excess of silver nitrate in the chloride determination (15), then

$$(Cl^-)_0 = N_{AgNO_3}\,[V_{AgNO_3\,(s)} - V_{AgNO_3\,(b)}] + (Cl^-)\,[(FeCNS^{+2})_t, \mu] \tag{18}$$

where the subscripts *s* and *b* represent titrations of the sample and a blank of the same excess of thiocyanate, respectively. In other words, a titration in conformance with the three conditions given above would yield results which are low by only the free chloride-ion concentration, which for most cases is negligible.

The absolute magnitude of the operator determinate end-point error, $F[(\mathrm{FeCNS}^{+2})_t, \mu]$, was evaluated in the following manner: rewriting (17), the following expression was obtained

$$V_{\mathrm{KCNS}} = \frac{N_{\mathrm{AgNO_3}}}{N_{\mathrm{KCNS}}} V_{\mathrm{AgNO_3}} + \frac{F[(\mathrm{FeCNS}^{+2})_t, \mu]}{N_{\mathrm{KCNS}}} \tag{19}$$

By plotting volume of KCNS *vs.* volume of $AgNO_3$, a straight line, the slope of which is $N_{\mathrm{AgNO_3}}/N_{\mathrm{KCNS}}$ and intercept is $F[\mathrm{FeCNS}^{+2})_t, \mu]$, is obtained.

TABLE I

EVALUATION OF THE OPERATOR DETERMINATE END-POINT ERROR

0.05101 N AgNO₃		*0.05646 N AgNO₃*	
V_{KCNS} *ml*	$V_{\mathrm{AgNO_3}}$ *ml*	V_{KCNS} *ml*	$V_{\mathrm{AgNO_3}}$ *ml*
1.77	1.99		
1.77	2.02	4.61	5.00
2.50	2.94	4.61	5.00
2.65	3.14	4.63	5.00
4.81	5.77	4.65	5.00
5.07	6.10	9.16	10.00
7.82	9.48	9.17	10.00
7.90	9.60	9.17	10.00
9.86	12.00	9.18	10.00
9.91	12.10	22.61	25.00
12.32	15.04	22.62	25.00
12.39	15.11		
14.65	17.96		
14.79	18.04		
17.12	20.98		
17.19	21.04		

With 0.05101 *N* $AgNO_3$, $V_{\mathrm{KCNS}} = 0.81130$, $V_{\mathrm{AgNO_3}} = +0.116$
With 0.05646 *N* $AgNO_3$, $V_{\mathrm{KCNS}} = 0.89935$, $V_{\mathrm{AgNO_3}} = +0.127$

Table I lists the results obtained from titrations of varying amounts of $AgNO_3$ with KCNS, as well as the results obtained from least-squares analysis of the straight line produced from plotting V_{KCNS} *vs.* $V_{\mathrm{AgNO_3}}$. Two different silver nitrate solutions, of strengths 0.05101 *N* and 0.05646 *N*, were used. 0.122 ml is the average value of $F[(\mathrm{FeCNS}^{+2})_t, \mu]/N_{\mathrm{KCNS}}$. The pooled standard deviation of this result is 0.0126 ml. This is the amount of the thiocyanate solution required to obtain an end-point. The operator determinate end-point error is calculated to be $7.66 \cdot 10^{-6}$ moles.

From the slopes of the two curves, the normality of KCNS may be evaluated as follows:

when $$N_{\mathrm{AgNO_3}} = 0.05101, \quad \frac{N_{\mathrm{AgNO_3}}}{N_{\mathrm{KCNS}}} = 0.81130$$

then

$$N_{\mathrm{KCNS}} = 0.06287$$

and when

$$N_{AgNO_3} = 0.05646, \; \frac{N_{AgNO_3}}{N_{KCNS}} = 0.89935$$

then

$$N_{KCNS} = 0.06278$$

and it is found the normalities are in agreement by 1.4 parts per thousand.

It is interesting to compare the value of the operator determinate end-point error and the "end-point error" reported by other investigators. Several investigators[3,6,7] find that an analytical concentration of 10^{-5} M of thiocyanate ion is sufficient to produce a perceptible color in a solution containing approximately 0.015 M ferric ion and 0.6 M nitric acid. Using a concentration formation constant (at an ionic strength of 0.6 M) of 139 for the formation of ferric monothiocyanate ion[8,9], the theoretical amount of $FeCNS^{+2}$ necessary to be perceptible is about $6.7 \cdot 10^{-6}$ M. In the work presented in this paper the volume of solution was about 160 ml, hence the analytical concentration of thiocyanate that is necessary for an end-point is $4.8 \cdot 10^{-5}$ M, which leads to a calculated amount of $FeCNS^{+2}$ of about $2.3 \cdot 10^{-5}$ M, when the ferric concentration is 0.0067 M.

The fact that 3.4 times the amount of $FeCNS^{+2}$ is required in this work than others, may lie partly in the fact that the "end-point blank" is usually determined in solutions which do not contain nitrobenzene and silver chloride and silver thiocyanate precipitates. In the carefully executed work of SWIFT *et al.*[7], it was noted that the concentration of $FeCNS^{+2}$ required for end-point detection increased when a silver chloride precipitate was present, in fact at the optimum ferric concentration, a 1.95-fold increase is calculated. The work presented here is the only one in which the actual conditions of the end-point are entirely simulated.

A larger contribution to the increased amount of $FeCNS^{+2}$ required to reach end-point is probably due to lack of sensitivity of the eye of the operator. This is a factor which must be appraised for each operator as an individual.

It should be reported here that KEYS[10], by means of novel micromanipulations, was able to achieve a sensitivity of 0.001 mg of chloride in a 10-ml solution, which is equivalent to $3 \cdot 10^{-6}$ M, however, this only represents the reproducibility of his method; no attempts to evaluate the accuracy of the method were made.

EXPERIMENTAL PROCEDURE

This procedure takes advantage of the possibility of eliminating the operator determinate end-point error by specifying that the ratio of silver nitrate solution to potassium thiocyanate solution be determined with the same volume of potassium thiocyanate solution as will be employed in the subsequent analysis. The theory underlying this expedient has been discussed and summarized above (18).

Reagents

1. *Silver nitrate solution, 0.05 N.* Weigh approximately 8 to 9 g of dry, reagent-grade $AgNO_3$ to the nearest milligram and dissolve in distilled water; dilute to exactly one liter.

Calculate the normality as follows:

$$N = \frac{W_{AgNO_3}}{169.89}$$

where W_{AgNO_3} is the weight of silver nitrate. Freshly prepared solutions of silver nitrate in distilled water need not be standardized.

2. *Ferric alum indicator.* Dissolve 200 g of ferric ammonium sulfate in 300 ml of distilled water. Heat to the boiling-point and add 25 ml of reagent-grade nitric acid. Filter, cool, and store in a Pyrex bottle.

3. *Potassium thiocyanate solution, 0.05 N.* Dissolve 4.8 to 5.0 g of reagent-grade potassium thiocyanate in distilled water and dilute to one liter. Standardize this solution against standard silver nitrate as follows: Transfer 5.00 ml of 0.05 N $AgNO_3$ to a 500-ml Erlenmeyer flask, and add 150 ml of distilled water and 8 ml of 1 : 1 nitric acid. Add 1 ml of nitrobenzene, 1 to 2 ml of ferric alum indicator, and titrate with potassium thiocyanate solution to a permanent red-brown color. Calculate the normality of the potassium thiocyanate solution as follows:

$$N = \frac{V_{AgNO_3}}{V_{KCNS}} \times N_{AgNO_3}$$

Procedure

Transfer a weighed portion of the sample which contains 2 to 20 mg of chloride salt to a 500-ml Erlenmeyer flask and dissolve in 150 ml of distilled water; it is permissible to assist solution by heat. Add 8 ml of 1:1 nitric acid to the cold solution and mix well. From a 10-ml buret, add a measured excess of 5 ml of standardized 0.05 N silver nitrate solution and mix well; then add 1 ml of nitrobenzene, and vigorously swirl the flask in order to coagulate the precipitate. Allow the precipitate to settle and carefully add a little more 0.05 N silver nitrate solution to the supernatant liquid; if an excess has been added, no turbidity will appear. Again swirl the flask in order to coagulate the precipitate; the supernatant liquid must not be milky. The 5-ml excess of silver nitrate can not readily be estimated initially; however, with use of results of the initial titration, one can easily calculate the total amount of silver nitrate to give a 5-ml excess in succeeding titrations of the same sample.

Add 1 to 2 ml of ferric alum indicator and titrate with 0.05 N potassium thiocyanate solution to a permanent red-brown color.

Calculate the per cent chloride salt content as follows:

$$\%\ \text{chloride salt} = \frac{M\,(aA - bB)}{10W}$$

where, M = molecular weight of the chloride salt being titrated, 53.50 for ammonium chloride, or 74.56 for potassium chloride. a = normality of silver nitrate solution. b = normality of potassium thiocyanate solution. A = volume of silver nitrate solution, (ml). B = volume of potassium thiocyanate solution, (ml). W = weight of sample, (g).

RESULTS

A summary of results of chloride determinations of synthetic chloride-in-ammonium nitrate and ammonium perchlorate mixtures is shown in Table II. The method recommended above for the calculation of the chloride content was not used, but rather the introduction of the calculated operator determinate end-point error (calculated above) as well as the calculated potassium thiocyanate normality into eqn. 15 to arrive at an equivalent "net" volume of silver nitrate consumed was used.

TABLE II

VOLHARD DETERMINATION OF SMALL CHLORIDE CONTENTS IN AMMONIUM NITRATE AND AMMONIUM PERCHLORATE

Salt	*NH_4Cl taken mg*	*$AgNO_3$ ml*	*KCNS ml*	*Net $AgNO_3$ ml*	*NH_4Cl found mg*	*Error mg*
None	0.00	5.01	4.62	0.01	0.03	+0.03
None	3.89	5.09	3.55	1.28	3.87	−0.02
None	9.73	8.77	5.12	3.21	9.70	−0.03
None	12.16	10.00	5.48	4.04	12.20	+0.04
None	19.08	9.91	3.34	6.33	19.12	+0.04
None	38.92	19.31	5.90	12.85	38.82	−0.10
30.0 g NH_4NO_3	0.00	5.04	4.60	0.06	0.18	+0.18
30.0 g NH_4NO_3	3.89	5.12	3.53	1.33	4.02	+0.13
30.0 g NH_4NO_3	3.82	4.19	2.72	1.30	3.93	+0.11
30.0 g NH_4NO_3	4.85	5.43	3.55	1.62	4.89	+0.04
30.0 g NH_4NO_3	7.27	6.54	3.79	2.46	7.43	+0.16
30.0 g NH_4NO_3	9.70	9.08	5.37	3.24	9.79	+0.09
30.0 g NH_4NO_3	11.46	7.27	3.20	3.85	11.63	+0.17
30.0 g NH_4NO_3	19.10	9.34	2.80	6.36	19.21	+0.11
24.4 g NH_4ClO_4	0.00	5.00	4.58	0.04	0.12	+0.12
22.1 g NH_4ClO_4	4.86	10.00	7.62	1.66	5.01	+0.15
23.8 g NH_4ClO_4	6.08	5.00	2.87	1.94	5.86	−0.20
26.9 g NH_4ClO_4	7.30	7.00	4.30	2.35	7.10	−0.20
23.8 g NH_4ClO_4	12.16	10.00	5.53	3.98	12.02	−0.08
26.0 g NH_4ClO_4	12.16	10.00	5.43	4.10	12.39	+0.23

$N_{AgNO_3} = 0.05646$; Net $V_{AgNO_3} = V_{AgNO_3} - 1.112\ (V_{KCNS} - 0.12)$

As mentioned previously, this result should be low by the amount of free chloride in the solution at the end-point. For most cases of the normal Volhard titration (ionic strength about 0.6 M), $(Cl^-)F(FeCNS^{+2})$ is negligible, however, this has not been ascertained at high ionic strengths. In particular, when small amounts of chloride (50–500 p.p.m.) are to be determined with reasonable accuracy, the required sample size becomes very large and the ionic strength will be greater than 4 M. Strictly speaking, it is necessary to standardize the potassium thiocyanate solution at this high ionic strength. However, by recognizing the fact that although the activity coefficients evaluated at 0.6 M and 4.3 M are considerably different, the ratios of activity coefficients at these two ionic strengths are not too different. The studies presented here were facilitated by making an approximation that the activity coefficient ratios are identical. The value of the operator determinate end-point error was evaluated at the usual ionic strength (about 0.6 M), and this value was utilized in the calculation of chloride contents titrated in media of high ionic strengths (up to 4.3 *M*). The results of these studies show that the amount of free chloride ion in solution at the end-point is negligible with respect to the concentration level of chloride present in the sample, or small enough to be masked with the indeterminate error of the measurement. Consequently, the approximation of constant activity coefficient ratios at ionic strengths of 0.6 *M* and 4.3 *M* proves to be valid, or if there is any discrepancy it is small enough to be hidden in the indeterminate error of the measurements.

Slightly high results of titrations of chloride in ammonium nitrate media were obtained; hence a small "salt effect" is indicated. However, the accuracy at this concentration level of chloride ion is adequate for most purposes. Because a 0.1-ml change in the net volume of silver nitrate leads to a change of 0.30 mg of ammonium chloride, the apparent "salt effect" discerned could easily be attributed to reproducibility variations; however, the constancy of direction of this variation affirms the belief of a small "salt effect". When expressed in absolute percent, chloride contents of 0.000 to 0.064% were determined with an average error of 0.0004%.

The randomness of direction of the apparent error of the titration of chloride in ammonium perchlorate infers that there is no "salt effect." The apparent error of this titration is greater than that obtained when titrating in ammonium nitrate media, but considering the low chloride ion level, the accuracy is quite satisfactory. When expressed as absolute per cent ammonium chloride, contents of 0.000 to 0.051% were determined with an average error of 0.0007%.

TABLE III

VOLHARD DETERMINATION OF SMALL CHLORIDE CONTENTS IN POTASSIUM PERCHLORATE

Salt	*KCl taken mg*	*$AgNO_3$ ml*	*KCNS ml*	*Net $AgNO_3$ ml*	*KCl found mg*	*Result*		
						Avg mg	*s[a] mg*	*Error mg*
None	2.89	6.54	4.79	0.78	2.97			
		7.51	5.61	0.74	2.81			
		4.08	2.81	0.77	2.93	2.90	0.08	+0.01
None	7.23	6.36	3.76	1.87	7.11			
		6.73	4.05	1.89	7.19			
		5.05	2.72	1.85	7.04	7.11	0.08	—0.12
8.0 g $KClO_4$	0.00	4.80	4.05	—0.04	—0.15			
		5.06	4.27	—0.08	—0.30			
		5.45	4.56	—0.02	—0.08	—0.18	0.11	—0.18
8.0 g $KClO_4$	2.89	4.05	2.85	0.69	2.62			
		4.10	2.88	0.70	2.66			
		6.14	4.50	0.74	2.81	2.70	0.10	—0.19
8.0 g $KClO_4$	7.23	5.07	2.75	1.83	6.96			
		6.45	3.92	1.77	6.73			
		5.77	3.31	1.84	7.00	6.90	0.15	—0.33

$N_{AgNO_3} = 0.05101$; Net $V_{AgNO_3} = V_{AgNO_3} - 1.233\ (V_{KCNS} - 0.12)$

[a] Standard deviation

The results of titrations of chloride determinations of synthetic chloride-in-potassium perchlorate mixtures is shown in Table III. Because of the sparing solubility of potassium perchlorate, the sample was dissolved in 200 ml of water at 50°, then the solution was allowed to cool to room temperature; potassium perchlorate crystals separate. The chloride content of this mixture was then determined by the procedure above. As would be expected from coprecipitation of chloride within the crystals of potassium perchlorate, the results of this determination are all low. The achieved accuracy is not as great as anticipated, but the results are acceptable. When expressed as absolute per cent potassium chloride, contents of 0.000 to 0.090 were determined with an average error of 0.0030% and reproducibility of 0.0015%. Another adaptation of the Volhard procedure was examined and abandoned; namely, addition of excess silver nitrate to the hot solution of potassium chloride and perchlorate. Coprecipitation of the excess silver nitrate occurred to such a degree that results comparable to those obtained when handling cool solutions (as above) were observed.

In conclusion, this study has shown that good results for the Volhard determination of small amounts of chloride ion in oxidizers can be achieved if the ratio of strengths of the potassium thiocyanate and silver nitrate solutions and the determination of the chloride are 1) carried out by the same operator and 2) exactly the same number of milliliters of potassium thiocyanate are used in each instance.

SUMMARY

The applicability of the Volhard titration to the determination of small amounts of chloride in solutions of high ionic strength has been examined. A rigorous derivation of the operator determinate end-point error, which is applicable to all analyses involving back-titrations and visual end-point detection, is presented together with a method for its empirical evaluation. Employ of the operator determinate end-point error has enabled determination of small amounts of chloride (0.00 to 0.090%) in ammonium nitrate, ammonium perchlorate, and potassium perchlorate with an average absolute error of 0.0004%, 0.0007%, and 0.0015%, respectively.

RÉSUMÉ

Les auteurs ont appliqué la méthode de VOLHARD au dosage de faibles teneurs en chlorure dans des solutions de force ionique élevée. On a pu doser des teneurs en chlorure de 0.000 à 0.09% dans le nitrate d'ammonium, le perchlorate d'ammonium et le perchlorate de potassium, avec un erreur de 0.0004%, 0.0007% et 0.0015%, respectivement.

ZUSAMMENFASSUNG

Es wird die Anwendung der Titrationsmethode nach VOLHARD zur Bestimmung kleiner Mengen von Chlorid in Gegenwart hoher Jonenkonzentrationen beschrieben und auf die einzuhaltenden Bedingungen hingewiesen.

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ANALYTICAL CHEMISTRY OF ZIRCONIUM

I. *o*-CRESOTIC ACID AND 4-AMINOSALICYLIC ACID IN THE DETERMINATION OF ZIRCONIUM

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Among the more important methods for the determination of zirconium are the gravimetric procedures involving precipitation of zirconium with cupferron[1], phosphate[2], mandelic acid[3], *m*-dinitrobenzoic acid[4], some phenolic acids[5] and *m*-cresoxy acetic acid[6]. To these may be added *o*-cresotic acid and 4-aminosalicylic acid. The precipitate is voluminous and settles quickly.

EXPERIMENTAL

Reagents

o-Cresotic acid (sodium salt) recrystallised; 4-amino salicylic acid (sodium salt) B.D.H.; zirconyl chloride, E. Merck, G.R.

Determination of zirconium

To the hot (80°) solution is added a 1% solution of the precipitant until precipitation is complete. The precipitate is digested for 10 min, filtered through Whatman paper No. 42, washed with hot water, dried and finally ignited to oxide before weighing. A few representative results are shown in Table I.

TABLE I

o-Cresotic acid		*4-Aminosalicylic acid*	
ZrO_2 taken (mg)	*ZrO_2 found (mg)*	*ZrO_2 taken (mg)*	*ZrO_2 found (mg)*
2.464	2.440	2.464	2.400
12.320	12.280	12.320	12.180
24.640	24.580	30.800	30.800
123.220	123.180	123.220	123.080
246.440	246.380	246.440	246.300

Both *o*-cresotic acid and 4-aminosalicylic acid proved to be efficient precipitants but *o*-cresotic acid was the more sensitive. The precipitate with *o*-cresotic acid was much more granular and easily filterable than that with 4-aminosalicylic acid.

Effect of hydrogen ion concentration on precipitation

In order to compare the efficiency of these acids at different hydrogen ion concentrations zirconium was determined at different pH values which were obtained by the addition of sodium acetate buffers. The results are shown in Table II.

TABLE II

pH	*ZrO_2 taken (mg)*	*ZrO_2 found (mg)*	
		o-Cresotic acid	*4-Aminosalicylic acid*
1.4	24.64	24.58	24.68
3.3	31.40	31.38	31.38
4.6	31.40	31.28	31.28
5.0	31.40	31.38	31.08
5.4	31.40	31.38	31.18

It can be seen that the recoveries of zirconium with 4-aminosalicylic acid decreased as the pH of the solution increased; the optimum pH range was 1.4–3.3. In the case of *o*-cresotic acid precipitation was quantitative at all pH values studied.

Determination of zirconium in presence of other ions

Ions such as bismuth(III), chromium(III), cerium(IV), manganese(II), molybdenum(VI) and vanadium(IV) did not interfere in these determinations of zirconium. But it is not possible to separate zirconium from thorium, the latter being quantitatively precipitated at all pH values. Double precipitation is needed if iron(III), copper(II) or uranyl ions are present as these form coloured complexes in solution.

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SUMMARY

o-Cresotic acid and 4-aminosalicylic acid are suitable for quantitative precipitation of zirconium; the precipitate is ignited and weighed. The optimum pH ranges are 1.4–5.4 and 1.4–3.3, respectively.

RÉSUMÉ

L'acide *o*-crésotique et l'acide amino-4-salicylique ont été utilisés avec succès pour le dosage gravimétrique du zirconium.

ZUSAMMENFASSUNG

o-Kresotinsäure und Amino-4-salicylsäure eignen sich zur gravimetrischen Bestimmung von Zirkonium.

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ANION EXCHANGE STUDIES OF URANIUM(VI) IN SULPHATE AND CARBONATE SOLUTIONS

SEPARATION FROM MIXTURES

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Uranium(VI) forms strong anionic complexes of the type $[UO_2(SO_4)_2]^{-2}$ and $[UO_2(SO_4)_3]^{-4}$ in sulphuric acid solutions; the formation constants for these complexes are 350 and 2500 respectively[1]. The anionic carbonate complex $[UO_2(CO_3)_3]^{-4}$ is much stronger, hence many ion exchange separations of uranium from commonly associated cations are possible. PREUSS AND KUNIN[1], and GRINSTEAD *et al.*[2] recovered uranium from carbonate and sulphate leach systems. BANERJEE AND HEYN[3] separated uranium from bismuth by anion exchange in sulphuric acid solution, at pH 1.0 – 1.5. Using essentially the same principle, SUSIC[4] worked out separation methods of uranium from cerium, alkali metals, and a few divalent metals. MURTHY[5] employed a carbonate medium for the anion-exchange separation of uranium from vanadium; vanadate was adsorbed along with the uranium complex, but was removed by elution with sodium carbonate solution and finally uranium was eluted with sodium chloride solution. Uranium(VI) also forms anionic chloro- and nitrato-complexes[6,7], which permits anion exchange separations of uranium from vanadium, iron etc.

However, systematic anion-exchange studies of uranium are lacking. The present paper describes the anion exchange behaviour of uranium(VI) in sulphate and carbonate systems, which are the two principal leach liquors of uranium. The strongly basic, quaternary ammonium type anion exchanger, Dowex 21K, was employed. Hydrochloric, nitric, sulphuric and perchloric acids and sodium chloride, ammonium chloride, sodium nitrate and sodium sulphate were studied as eluting agents. Uranium was separated from the important fission product elements *e.g.*, cerium, zirconium, caesium, silver and cadmium, from vanadium and also from phosphate and molybdate.

APPARATUS AND REAGENTS

Apparatus

Ion-exchange column and Cambridge pH meter.

The ion-exchange column was similar to that previously described[8]; a resin bed, 1.4 × 14.5 cm, was used.

Reagents

The chemicals used were of reagent grade, unless otherwise specified.

A uranium solution was prepared from uranyl nitrate hexahydrate (Mallinckrodt A.R.) and standardized by the usual oxine method. For ion-exchange runs, *ca.* 25 mg of uranium was taken.

Dowex 21K (Dow Chemical Cy., Midland, Mich., U.S.A.), 50–100 mesh, chloride-form anion exchange resin was pre-treated by alternate washing with 1 *N* hydrochloric acid, water and 0.5 *N* sodium hydroxide followed by water. After being slurried into the column, it was washed at a flow-rate of 2 ml/min with 1 *N* hydrochloric acid and then with water till the resin bed was free from chloride. For ion-exchange runs in sulphate or carbonate medium, the resin was converted to the appropriate form by washing with 10% sulphuric acid or 10% sodium carbonate solution and washed with distilled water till free from sulphate or carbonate.

EXPERIMENTAL, RESULTS AND DISCUSSION

Ion-exchange behaviour studies

A. Sulphate system. An aliquot of the uranyl nitrate solution was evaporated to fumes with sulphuric acid in a 50-ml beaker so that uranyl sulphate was formed. This was dissolved in a little water and the pH adjusted to 1.0–1.5 with 0.01 *N* sulphuric acid and 0.01 *N* sodium hydroxide by means of a pH meter. This solution, containing an anionic sulphate complex of uranium, was passed through the resin bed at a rate of 1 ml per minute. The resin was washed with 50 ml of water and then with 200 ml of the different eluants at the same flow rate. The eluants were hydrochloric acid (0.25, 0.50, 1.0 and 2.0 *M*), nitric acid (0.25, 0.50, 1.0 and 2.0 *M*), perchloric acid (0.25, 0.50, 1.0 and 1.5 *M*), sulphuric acid (1, 2 and 3 *M*), ammonium chloride (1, 3, 5 and 10%), citric acid (pH 5.0 – 5%) and sodium hydroxide (1%). The effluent batch (200 ml) was evaporated nearly to dryness with 5 ml of sulphuric acid and 2 ml of perchloric acid (70%) to destroy any organic matter from the resin, and uranium was determined gravimetrically by the oxine method.

TABLE I

BEHAVIOUR OF THE ANIONIC SULPHATE COMPLEX OF URANIUM(VI) TOWARDS VARIOUS ELUTING AGENTS

Uranium = 24.76 mg. Wt. of resin = 9.5420 g (oven-dried)

No.	*Eluting agents*	*Eluant concentration, M*	*Total uranium recovery, %*
1	$HClO_4$	0.25	106.2
	$HClO_4$	0.5	97.6
	$HClO_4$	1.0	97.0
	$HClO_4$	1.5	96.8
2	HNO_3	0.25	96.8
	HNO_3	0.5	100.3
	HNO_3	1.0	103.9
	HNO_3	2.0	93.5
3	H_2SO_4	0.25	95.0
	H_2SO_4	1.0	98.5
	H_2SO_4	2.0	103.8
	H_2SO_4	3.0	100.9
4	HCl	0.25	96.0
	HCl	0.5	95.8
	HCl	1.0	104.4
	HCl	2.0	80.0
5	NH_4Cl	1%	79.9
	NH_4Cl	3%	83.6
	NH_4Cl	5%	105
	NH_4Cl	10%	100.5
6	NaOH	1%	2.2

The results (Table I) show that essentially quantitative elution was possible with 200 ml of perchloric acid (0.25 – 1.5 *M*), nitric acid (0.25 – 2.0 *M*), sulphuric acid

(0.25 – 3 *M*) and hydrochloric acid (0.25 – 1.0 *M*). The elution was incomplete with higher concentrations of hydrochloric acid presumably owing to the formation of the $[UO_2Cl_4]^{-2}$ complex[9]. Citric acid at pH 5.0 (5%), tartaric acid (5%) and sodium hydroxide (0.5%) failed to elute uranium; with 1% sodium hydroxide only about 2% uranium was recovered. Ammonium chloride (5–10%) gave quantitative recovery of uranium. For routine work perchloric acid (0.5 – 1.0 *M*) is preferred because it is easily volatilized in the assaying step and does not form anionic chloro-complexes. The eluting agents may be arranged in order of decreasing efficiency: $ClO_4^- > NO_3^{-2} > SO_4^{-2} > Cl^- > OH^-$. This falls in line with the qualitative series[10] expressing the decreasing selectivity of Dowex 21K for various anions: $CNS^- > I^- > NO_3^- > Br^- > CN^- > HSO_4^- \simeq HSO_3^- > NO_2^- > Cl^- > HCO_3^- > CH_3COO^- > OH^- > F^-$.

B. Carbonate system. The anionic carbonate complex, $[UO_2(CO_3)_3]^{-4}$ was prepared as follows. A known aliquot of uranyl nitrate solution was converted to sulphate as before and dissolved in water and the solution was carefully neutralised with solid sodium carbonate. Then 5 g of sodium carbonate was added, and the solution was diluted to 50 ml, boiled if necessary, and cooled to room temperature. The uranium solution was run through the resin column at a rate of 1 ml per minute. The resin was washed with 50 ml of water and 200 ml of the eluant was passed at a rate of 2 ml per minute. The eluants were sodium chloride (2, 4, 5, 10%), ammonium chloride (5, 10%), sodium nitrate (5, 10%) and sodium sulphate (10%). The effluent batch was boiled with 10 ml of 8 *N* nitric acid to expel carbon dioxide, cooled and neutralised with ammonia and finally uranium was analysed as the oxinate.

Sodium chloride (5–10%), ammonium chloride (10%) and sodium nitrate (5–10%) permitted quantitative elution. Lower concentrations of these eluants and also sodium sulphate — even 10% — gave incomplete elution (Table II).

TABLE II

BEHAVIOUR OF ANIONIC CARBONATE COMPLEX OF URANIUM TOWARDS VARIOUS ELUTING AGENTS

Resin = 9.5420 g (oven dried)

No. agents	*Eluting agents*	*Eluant concentration, %*	*Total uranium recovery, %*
1	NaCl	2[a]	35.2
	NaCl	4	58.7
	NaCl	5	96.8
	NaCl	10	102.5
2	NH_4Cl	5	51.8
	NH_4Cl	10	98.5
3	$NaNO_3$	5	105.5
	$NaNO_3$	10	95.8
4	$Na_2SO_4 \cdot 10\,H_2O$	10	10.8

[a] Elution with 300 ml

Ion-exchange separations

A. Sulphate system. The separations of uranium from zirconium, cerium, caesium, silver, cadmium and vanadium are based on the fact that the anionic sulphate complex of uranium(VI) is quantitatively retained by the anion exchanger, whereas the cations which do not form anionic complexes pass through the column.

In each case the mixture was processed as in the above preparation of the anionic uranium sulphate complex. After the adsorption, the column was washed with 50 ml of 0.05 *M* sulphuric acid and 50 ml of water; finally uranium was eluted from the resin with 200 ml of 0.5 *M* perchloric acid and determined as described above.

The results (Table III) show that, except in mixtures containing thorium, essentially quantitative separations were obtained. Thorium was adsorbed under the same conditions as uranium[11]. High results were obtained with U : Th ratios greater than 10 : 1 owing to coelution of thorium with uranium. The separation of these metals in any ratio seems to be possible by selective elution; uranium is first eluted with *ca.* 0.25 *M* sulphuric acid and thorium is then eluted with 1 *M* or stronger acid. However this was not further examined, since cation-exchange separation[8] is much simpler. Those cations which give precipitates in sulphate medium interfere, *e.g.* barium, strontium, calcium and lead. Anions are adsorbed with uranium. However, the method may be extended to cover a large number of cations, and may be used for the purification of uranium from commonly associated cations.

TABLE III

ION-EXCHANGE SEPARATION IN SULPHATE SYSTEM

U = 23.77 mg

No.	*Foreign ion added, mg*		*Uranium recovery %*
1	Zr	24.10	95.9
2	Zr	2.4	103.4
3	Zr	95.0	106.8
4	Ce(IV)	22.32	106.3
5	Ce(IV)	2.8	96.7
6	Ce(IV)	44.6	100.4
7	Cs	24.0	105.3
8	Cs	100.0	102.9
9	V(V)	24.5	96.5
10	V(V)	2.5	100.6
11	Ag	2.5	101.0
12	Ag	25	103.4
13	Cd	2.5	101.4
14	Cd	25.5	99.9
15	Th	2.3	109.0
16	Th	22.5	160.4

B. Carbonate system. Many metal ions, particularly those of the heavy metals, precipitate in carbonate medium, and their separation from uranium is not possible. However, uranium can be separated from commonly associated anions, *e.g.* phosphates and other anions, *e.g.* molybdate, by selective elution. The method is virtually an extension of that proposed by MURTHY[5]. Phosphate or molybdate was adsorbed along with uranium and was removed with 10% sodium carbonate; finally uranium was eluted with 5% sodium chloride.

The free acid in the uranium solution (sulphate) was neutralized with sodium carbonate, the desired anion was added and the mixture was made 10% with respect to sodium carbonate as described before. The solution was run through the column at a flow rate of 1 ml per minute. The bed was washed with 30 ml of 10% sodium carbonate at 2 ml per minute. The phosphate or molybdate was eluted with 200 ml of 10% sodium carbonate and uranium was then eluted with 200 ml of 5% sodium chloride at 2 ml per minute. The last traces of phosphate or molybdate were removed before elution of uranium began. The separations obtained are shown in Table IV. Large scale separations could be effected with larger ion-exchange columns.

TABLE IV

ION-EXCHANGE SEPARATIONS IN CARBONATE SYSTEM

$U = 23.77$ mg

No.	*Foreign ion added, mg*		*Uranium found mg*	*Uranium recovery %*
1	PO_4^{-3}	25	22.98	96.7
2	PO_4^{-3}	250	22.70	95.4
3	PO_4^{-3}	100	24.50	102.9
4	$Mo_7O_{24}^{-6}$	24	23.90	100.4
5	$Mo_7O_{24}^{-6}$	240	23.52	98.9

The results in Tables I–IV are reproducible to within ± 5%

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SUMMARY

The anion-exchange behaviour of uranium(VI) in two important leach systems, sulphate and carbonate, is described. Hydrochloric, nitric, sulphuric and perchloric acids and sodium chloride, ammonium chloride, sodium nitrate and sodium sulphate were tested as eluants on a Dowex 21K column. In the sulphate system uranium is separated from fission product elements, *e.g.* cerium, zirconium, caesium, silver, cadmium, and from vanadium; in the carbonate system, it is separated from phosphate and molybdate.

RÉSUMÉ

Une étude a été effectuée sur le comportement chromatographique de l'uranium(VI). On a pu, en solution sulfatée, le séparer sur colonne de Dowex 21K (échangeur d'anions) d'avec les éléments de produit de fission importants, Ce, Zr, Cs, Ag, Cd et V et, en solution carbonatée, d'avec phosphate et molybdate.

ZUSAMMENFASSUNG

Eine Untersuchung über das chromatographische Verhalten von Uran(VI) hat gezeigt, dass es sich von den wichtigsten Spaltprodukten (Ce, Zr, Cs, Ag, Cd und V) über einer Dowex 21K Kolonne mit Sulfatlösung trennen lässt. Mit Karbonatlösung kann eine Trennung von Phosphat und Molybdat erzielt werden.

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CHROMATOGRAPHIC SEPARATION OF INORGANIC ANIONS ON SPECIALLY PREPARED CALCIUM SULPHATE STICKS

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Inorganic ions can be separated by a simplified chromatographic technique with various adsorbents[1]; of these, calcium sulphate in the form of specially prepared sticks is most effective for obtaining rapid separations, the identification being complete in less than 10 min. The method has already been used for the qualitative separation of about a dozen cations[2,3].

This paper records the extension of the method to the rapid qualitative separation of inorganic anions.

EXPERIMENTAL

The sticks were prepared as previously described[3], except that the proportion of calcium sulphate ($CaSO_4 \cdot 2H_2O$) to plaster of Paris was 45 : 55 instead of 55 : 45. The technique was similar to that described previously[3].

RESULTS

Separation of phosphate from phosphite

Neutral solutions (pH 6.5–7) were used. After being washed with water, the stick was made just dry and sprayed with silver nitrate reagent. A distinct yellow band appeared a little above the point of application of the test solution. After 2 minutes, a broad black band appeared at quite a large distance above the yellow band. The first patch of white silver phosphite at this position could scarcely be seen until it became reduced to black metallic silver.

Separation of arsenate from arsenite

This was done in the same way as the phosphate–phosphite separation. Two distinct bands appeared. The chocolate arsenate band appeared just above the application point while the yellow arsenite band appeared farther up the stick.

Separation of arsenate from phosphite

In this case, after spraying with silver nitrate, the chocolate arsenate band appeared just above the application point while the broader black phosphite band was the same as mentioned above.

Separation of arsenite from phosphite

Again, the same procedure was used. A quite broad yellow band of arsenite appeared a little above the application point and after about two minutes a distinct broader black band of phosphite appeared considerably above it.

Separation of thiosulphate from thiocyanate

The stick was washed with water containing 10% acetone; water alone caused imperfect separation. A mixture (1 : 1) of 0.2 N ferric nitrate and 0.2 N silver nitrate was used as the spray. The bands were broad and clearly separated. The red ferric ferri-thiocyanate band lay above the black silver sulphide band, the sulphide being formed by the rapid decomposition of silver thiosulphate. The latter band appeared just above the application point.

Separation of ferricyanide from thiocyanate

The stick was washed with water, allowed almost to dry, and sprayed with ferric chloride reagent. Two equally broad bands were obtained, one red and one brown. The stick was then sprayed with a dilute solution of ferrous ammonium sulphate. The brown band nearest the application point turned deep blue. The red ferric ferri-thiocyanate band remained unaltered and could be confirmed by bleaching with mercuric chloride solution.

Separation of ferrocyanide from thiocyanate

Water alone was used for washing. Distinct blue and red bands were formed with ferric chloride reagent. The blue band appeared a little above the application point with the red band a little above it. The latter could be bleached with mercuric chloride solution.

Separation of ferrocyanide from ferricyanide

The wash water contained 15% *n*-propyl alcohol; water alone gave imperfect separation. The stick was sprayed with copper sulphate reagent. Two bands appeared, upper chocolate and lower green, separated by a considerable distance. The green band appeared just above the application point and the chocolate band considerably farther up. Ferric chloride was also used to identify the separated ions as blue and brown bands. When the moist stick was treated with sulphur dioxide the brown band turned blue.

SUMMARY

Specially prepared calcium sulphate sticks are suitable adsorbents in the chromatographic separation of inorganic anions. Separations of various binary mixtures of phosphate, phosphite, arsenate, arsenite, thiosulphate, thiocyanate, ferricyanide and ferrocyanide are possible.

RÉSUMÉ

Une méthode chromatographique est proposée pour la séparation d'anions, utilisant des baguettes de sulfate de calcium, spécialement préparées.

ZUSAMMENFASSUNG

Beschreibung einer chromatischen Methode zur Trennung der Anionen mit Hilfe von Calciumsulfat in Form von Stäbchen.

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THE DETERMINATION OF STRONTIUM IN ROCKS AND BIOLOGICAL MATERIALS

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INTRODUCTION

Owing to the biological importance of strontium-90, it is desirable that the path of natural strontium from the soil through vegetable matter and animals should be understood. The administration of radioactive tracers to living subjects can give only relative information on retention, distribution, and excretion and can seldom give the absolute concentration of the natural element. Therefore there is a need for accurate strontium analyses at trace levels in a wide range of botanical and biological specimens, as well as in soils and rocks. Emission spectrography is a suitably rapid technique, but there is always the possibility of unsuspected suppression or enhancement of emitted lines by other constituents in the sample. It is therefore desirable that the reference standards for spectrographic analysis shall be as nearly as possible identical to the sample, both in chemical composition and physical form. Both neutron activation and stable dilution analyses offer ways of determining the strontium content of materials with sufficient accuracy and precision so that these may be used later as reference standards for spectrographic work.

A number of authors have established methods for determining strontium by neutron activation. BROOKSBANK, LEDDICOTE AND MAHLMANN[1] have studied strontium in animal tissues, while SOWDEN AND STITCH[2] have published a series of neutron activation analyses carried out on samples of human bone. BOWEN[3] and BOWEN AND DYMOND[4] have used neutron activation for determining strontium in sea water, marine organisms, plants and soils. HUMMEL AND SMALES[5] obtained a slightly lower figure than that reported by BOWEN AND DYMOND for strontium in sea water and confirmed it by stable isotope dilution analysis. HARRISON AND RAYMOND[6] developed an analytical scheme for the rapid determination of strontium in excreta using the induced strontium-87m isotope.

Because most of these methods have been restricted in their application, we have sought to establish a radiochemical procedure which is adequate for the assay of natural strontium in a wide variety of matrices and to compare these results with an independent series of figures obtained by stable isotope dilution analysis.

Hitherto, the stable isotope dilution technique has been concerned mainly with geological age work, but its use for the determination of strontium in standard rock samples has been reported[7,8]. The method is based upon the addition of a known quantity of enriched strontium-84 tracer to the sample, followed by the estimation of the quantity of normal strontium (mainly ^{88}Sr) from the change in the ^{84}Sr/^{88}Sr isotope ratio. Interference can be caused only by elements with isobars. In this case the isobaric elements are krypton and rubidium. Krypton does not produce ions with the thermal emission source used for strontium; rubidium has isotopes of mass 85 and 87 only, and so does not interfere with the determination of the ^{84}Sr/^{88}Sr isotope ratio unless it is present in very large quantities. Thus the only likely source of systematic error is contamination, but with fairly simple precautions this may be restricted to 0.3 μg, and the appropriate blank correction applied.

NEUTRON ACTIVATION ANALYSIS

Outline of the methods

The strontium-89 isotope

This procedure is applicable to the determination of strontium in rocks and minerals where an exceptional degree of radiochemical decontamination is required and where there may be some doubt whether the shortened scheme, using the strontium-87m isotope, will be adequate. The nuclear reaction is:

^{88}Sr(n,γ)^{89}Sr; ^{89}Sr $\rightarrow$ ^{89}Y (stable); activation cross-section, 0.005 barns.

Samples and strontium standards are sealed into silica phials and irradiated in the highest available neutron flux. The activated material is dissolved in the presence of carrier strontium. Successive treatments with fuming nitric acid precipitate the strontium and eliminate the bulk of the calcium and other interfering induced activities. Three pairs of scavenges follow: acid sulphide (antimony carrier), alkaline sulphide (cobalt carrier), and hydroxide scavenge (ferric iron carrier). The strontium is precipitated as the carbonate, converted to the nitrate, dissolved in water and fed to an ion-exchange column. Strontium, essentially free of calcium, is eluted chromatographically from the column and recovered from the appropriate fraction of the eluate by oxalate precipitation. After being washed, the strontium oxalate is dissolved, reprecipitated, washed, slurried on to an aluminium counting tray, dried under an infra-red lamp, weighed and beta-counted. The observed activity is corrected for chemical yield and compared with the activity of the strontium reference standards which have undergone the same irradiation and chemical treatment.

The radiochemical technique requires a period of about nine hours which is too long to permit the same separations to be used with adequate sensitivity for the shorter-lived (2.7 h) isotope, strontium-87m.

The strontium-87m isotope

The abbreviated procedure, using the strontium-87m isotope, is appropriate for botanical or biological specimens where the calcium/strontium ratio is not much greater than 1600:1. Other cations capable of high induced specific activities during a three hour irradiation may be present in amounts not greater than trace level. The nuclear reaction is:

^{86}Sr(n,γ)^{87m}Sr; ^{87m}Sr (isomeric transition) $\rightarrow$ ^{87}Sr(stable); activation cross-section 1.5 barns.

After irradiation for two and a half to three hours, the phials are opened and the contents dissolved in the presence of strontium carrier. Calcium is eliminated by a succession of four fuming nitric acid precipitations of strontium nitrate. Two scavenges with ferric hydroxide remove extraneous activity. The ion-exchange step is omitted and therefore radio-barium must be removed by duplicate precipitations with barium carrier. Strontium is recovered as the oxalate and prepared for beta-counting as in the ^{89}Sr method.

Experimental discussion

Samples need not be ashed before irradiation. Silica phials are most suitable for irradiations lasting more than a few hours, but shorter irradiations can be carried out successfully with the samples sealed in short lengths of polythene tubing. The low melting point of polythene is an advantage with biological samples, such as milk powder, which are likely to char at the higher temperatures needed to seal off a silica phial.

Each standard contains 100 μg of strontium (natural isotopic abundance) in the form of a 0.1-g aliquot of a solution of 1 mg strontium per ml. The standard solution is transferred into the weighed phials by a dropping pipette and rubber bulb. The pipettes are made with a slender tip lightly treated upon the outside with"Repelcote" (Hopkins and Williams Ltd.), or a similar solution of water-repellent silanes in carbon tetrachloride, to prevent the standard solution being drawn up between the walls of the phial and the pipette tip.

Decontamination from interfering radioactivity offers no problem with the exception of radio-calcium. The calcium/strontium ratio in bone ash is about 1600 and the ratio of the induced radioactivities will be approximately 4 at the time of beta-counting if the strontium-87m method is used. A decontamination factor of 10^3 for calcium-45 is therefore adequate. In the case of rocks analysed by the strontium-89 method, the calcium/strontium ratio may be in the vicinity of 2000 and the ratio of induced activities at the time of counting will then be about 5400. A decontamination factor of 10^7 for calcium-45 is the minimum acceptable for the strontium-89 method.

Three fuming nitric acid precipitations[9,10] of strontium nitrate (8 ml of fuming nitric acid to 5 ml of solution) give a separation from calcium with a decontamination factor of better than 1000 which is sufficient for the strontium-87m scheme; but nitric acid separations alone would be a tedious means of obtaining the decontamination factor of 10^7 which is necessary in the strontium-89 procedure. A chromatographic ion-exchange step is therefore added to purify the strontium from the last traces of calcium and obtain an overall decontamination factor of at least 10^7 from calcium-45.

LERNER AND RIEMAN[11] described the separation of calcium, strontium, and barium on a column of "colloidal Dowex-50" (less than 120 mesh) and their method has been modified to obtain a clear separation of small quantities on a very much smaller column. Addition of 0.05 M citric acid to 1 M lactic acid (pH adjusted to 7 with concentrated ammonium hydroxide) improves the behaviour of strontium on a 4 gram column of Zeo-Karb 225 (7 mm × 155 mm, 50 μ resin particles).

Four grams of air dried resin are weighed out and wetted with the eluent. When the resin has ceased to swell, it is slurried into the glass tube. The column is washed for an hour with the lactate–citrate eluent at 20ml/h and for another hour with demineralised water. If the column is not prepared in this manner, the separation of calcium and strontium becomes unpredictable. The active solution is fed on to the column as a neutral solution of nitrates and the column washed with two ml of water before beginning the elution. The exact positions of calcium and strontium were checked by using radio-tracers in preliminary experiments and a typical elution curve is shown in Fig. 1.

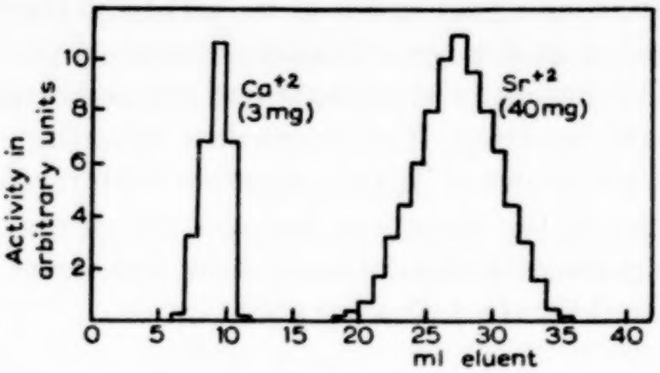

Fig. 1. The elution of calcium and strontium from a 7 mm × 155 mm columm of Zeo-Karb 225 (4 grams of dried resin) with 1 *M* ammonium lactate, 0.05 *M* ammonium citrate at pH 7.

The radiochemical purity of the separated strontium-87m sources can be demonstrated by following the decay of the isotope over at least ten half-lives. Irradiation induces a small proportion of strontium-89 and the activity due to this nuclide appears as a constant (54 day half-life) tail to the decay of the shorter-lived isotope. If the decay curves of the sample and standards plotted upon the same time base can be superimposed, they are of equal radiochemical purity. Subtraction of the "tail" from the decay curve should yield a linear decay curve on semi-logarithmic paper with a half-life very close to 162 min if no other impurities are present.

It is not practicable to prove the radiochemical purity of separated strontium-89 by recording the decay because the half-life is too long to give a decisive answer in a reasonable length of time. Instead, the beta-energies of the sample sources may be compared with the energy of the standards by measuring the source activity through a series of aluminium absorbers and plotting an "absorber curve", *i.e.* the logarithm of activity against absorber thickness. All the experimental curves were coincident with the curves obtained from pure strontium standards.

A few percent of radio-calcium shows up very clearly on an absorber curve by a well-defined increase in the negative slope in the region of 0.50 mg Al/cm^2. Emitters with beta-energies close to that of strontium-89 (1.46 MeV) will not be revealed.

Interfering nuclear reactions

There are several possible nuclear reactions (other than the *n,γ*-reaction on stron-

TABLE I

SIGNIFICANT STRONTIUM ISOTOPES ARISING FROM THE FISSION OF URANIUM-235 BY THERMAL NEUTRONS

Nuclide	*Half-life*	*Fission yield*	*Beta-energy MeV*	*Proportion*	*Gamma-energy MeV*	*Proportion*
Sr-89	54 day	4.8%	1.46	100%	—	—
Sr-90	28 y	5.9%	0.54	100%	—	—
Sr-91	9.7 h	5.9%	0.62	7%	1.413	7%
			1.09	33%	1.025	33%
			1.36	29%	0.747	7%
			2.03	4%	0.66	22%
			2.66	27%	0.64	33%
Sr-92	2.7 h	6.1%	?	100%	—	—

tium) which may produce radio-strontium: 1. Fission of uranium; 2. Fission of plutonium; 3. Fission of thorium; 4. *n,α* on zirconium; 5. *n,p* on yttrium.

The fission of uranium and plutonium is initiated by thermal neutrons, but the latter may be disregarded as it is an artificial element which is not likely to be met in natural samples. The fission of thorium[12] and the reported *n,α*-reactions on zirconium[13,14] require fast neutrons. The important strontium isotopes arising from fission of uranium-235 are shown in Table I together with related nuclear data[15].

The relative activities of the strontium isotopes which may be expected from the irradiation of a microgram of natural uranium in a thermal flux of 10^{12} neutrons/cm^2-sec can be calculated by the following equation:

$$\text{d.p.m./}\mu\text{g uranium} = 6.06 \times 10^5\, ø \left(1 - e^{-\frac{0.693t}{t_{\frac{1}{2}}}}\right)$$

where $ø$ is the fission yield of the nuclide sought, $t_{\frac{1}{2}}$ its half-life, and t the time of irradiation.

Calculated activities for strontium under two conditions of irradiation are given in Table II. Table III shows the strontium activity found experimentally and the ratio of the activities of irradiated strontium and fission product strontium. Interference by uranium is proportionately less by the strontium-89 method.

TABLE II

RELATIVE ACTIVITY OF STRONTIUM ISOTOPES ARISING FROM THE THERMAL NEUTRON FISSION OF URANIUM

Nuclide	*3-h irradiation and 10-h cooling period*	*14-day irradiation and 1-week cooling period*
^{89}Sr	44 d.p.m./μg U	3640 d.p.m./μg U
^{90}Sr	0.3 d.p.m./μg U	36 d.p.m./μg U
^{91}Sr	3380 d.p.m./μg U	(decayed)
^{92}Sr	1475 d.p.m./μg U	(decayed)
Totals	4899 d.p.m./μg U	3676 d.p.m./μg U

TABLE III

OBSERVED INDUCED ACTIVITY IN STRONTIUM AND THE ACTIVITY OF STRONTIUM ARISING FROM THE FISSION OF URANIUM

Irradiation and the analytical procedure	*Irradiated natural strontium*	*Fission product strontium*	*Activity ratio*
3-h irradiation ^{87m}Sr method of analysis with added sulphide scavenges	40 c.p.m./μg Sr	720 c.p.m. Sr/μg U	18.0
	62 c.p.m./μg Sr	1200 c.p.m. Sr/μg U	19.4
	30 c.p.m./μg Sr	580 c.p.m. Sr/μg U	19.3
14-day irradiation ^{89}Sr method of analysis	71 c.p.m./μg Sr	825 c.p.m. Sr/μg U	11.6
	65 c.p.m./μg Sr	714 c.p.m. Sr/μg U	11.0
	57 c.p.m./μg Sr	588 c.p.m. Sr/μg U	10.3
	20 c.p.m./μg Sr	220 c.p.m. Sr/μg U	11.0

The international standard granite, G-1 (see Table VII), contains 3.6 p.p.m. of uranium[16] and the same investigators report 0.5 p.p.m. of uranium in the diabase, W-1. The strontium content of these rocks is about 250 p.p.m. and 170 p.p.m. so the fission strontium correction is approximately 14% and 2.5% of the observed activity in the final sources respectively.

Similar comparisons were carried out with thorium, zirconium, and yttrium to determine the levels at which they interfere significantly with a strontium determination. If the acceptable interference level is taken to be 1% of the induced strontium activity, then the relative quantities of each element which can be tolerated without requiring a correction are shown in Table IV.

TABLE IV

THE RELATIVE QUANTITIES OF URANIUM, THORIUM, ZIRCONIUM AND YTTRIUM WHICH WILL CAUSE AN ERROR OF 1% IN THE DETERMINATION OF STRONTIUM BY NEUTRON ACTIVATION

14-day irradiation and 7-days cooling	Uranium	0.0009	times the weight of strontium
	Zirconium	180	times the weight of strontium
	Yttrium	3.3	times the weight of strontium
3-h irradiation and 10-h cooling	Uranium	0.00055	times the weight of strontium
	Thorium	0.4	times the weight of strontium
	Zirconium	750	times the weight of strontium
	Yttrium	250	times the weight of strontium

ANALYTICAL PROCEDURE

The strontium-89 activation procedure

Prepare irradiation phials and weigh 0.1–0.4 g of sample into each phial and seal it. Also prepare two or more standards each containing 100 μg of strontium (standard solution containing 1 mg Specpure strontium per ml). If uranium is present in the samples, prepare several uranium standards (5 μg uranium in solution). Clean the phials externally and pack into an irradiation can. Irradiate for 1–3 weeks at the highest available neutron flux and allow the induced activity to decay for several days before commencing the radiochemistry.

Open the phials and dissolve water or acid-soluble inorganic materials in 5 ml of strontium carrier solution (12 mg Sr/ml) and 1 ml of dilute nitric acid. Add 18 ml of fuming nitric acid. Chill the solution in an ice bath for five minutes before centrifuging. Discard the supernatant acid and dissolve the precipitate in 5 ml of water. Add 8 ml of fuming nitric acid, chill and centrifuge. Repeat the nitrate precipitation twice. If large quantities of sulphate are present in the sample, a carbonate metathesis step precedes the first nitrate precipitation to ensure exchange between radiostrontium and the carrier.

Wet-oxidise organic material by the procedure of G.F. SMITH[17]. First clean the irradiated silica phials externally by heating at 60–70° in a few hundred ml of water containing 20–30 g of strontium nitrate. Remove, rinse, and dry the phials. Relieve internal pressure by breaking the tip off the phial with forceps and then break open at the neck. Place the body of the phial and its contents in a 50-ml beaker containing 4 ml of 72% perchloric acid, 2 ml of concentrated nitric acid, 5 ml of strontium carrier solution, and two drops of 2 *M* sodium chromate solution as a catalyst. Heat cautiously on a hotplate to keep the reaction going steadily without loss by spraying or boiling. When all visible organic matter has been destroyed, remove the broken phial with a pair of glass forceps bent from 2 mm glass rod. Rinse the phial with a few drops of water on removal. Continue the oxidation until the solution changes colour from green to orange. Remove the beaker from the hotplate and cool before pouring the acid into a 50-ml centrifuge tube. Rinse the beaker once with 2 ml of water and add the water to the centrifuge tube. Rinse the beaker with 9 ml of fuming nitric acid, in small portions, and pour the rinsings into the tube, thus precipitating strontium nitrate. Chill the tube and its contents for five minutes in an ice bath. Centrifuge, and discard the acid. Dissolve the strontium nitrate in 5 ml of water. Add 8 ml of fuming nitric acid, chill, centrifuge, and repeat the nitrate precipitation twice to separate the strontium from radio-calcium.

Rock samples are attacked by a sodium peroxide frit.[18] Weigh 3 g of dry granular sodium peroxide into a 25-ml nickel crucible. Break open the irradiation phial and tap the contents into the crucible (Caution: radioactive dust). Mix well using a glass stirring rod 2 mm in diameter. Level the peroxide by tapping the side of the crucible then dust 1 g of sodium peroxide evenly over the surface which must be well covered if the frit is to be successful. Place the crucible in a muffle furnace at 480 ± 20° for twenty to thirty minutes. Remove the crucible from the furnace and plunge the lower half into a beaker of ice-cold water for a minute—a surface colour change indicates when the centre of the mass is cool. Turn the crucible upside down over the mouth of a 400-ml conical beaker containing the dissolving solution and tap the bottom sharply to release the cake. Prepare the dissolving solution as follows:
100 ml water (demineralised); 30 ml industrial methylated spirits; 10 ml concentrated hydrochloric acid; 5 ml strontium carrier solution (12 mg Sr/ml).

The peroxide frit dissolves without violence in the presence of the alcohol. If the reaction is too slow, reduce the quantity of alcohol. Gentle warming aids the final stage of dissolution, but the quantity of acid is sufficient for complete solution. Addition of excess acid will lead to the precipitation of silicic acid.

To remove silica, add 10–20 mg of iron to the warm solution and then add concentrated ammonium hydroxide slowly with stirring until slightly ammoniacal. Filter the precipitate immediately and rinse the beaker several times with water, pouring the rinsings through the filter paper. To the filtrate add 50 ml of 4 *N* sodium carbonate solution. Digest the precipitate on a warm hotplate until the bulk of it begins to settle. Centrifuge. Discard the supernatant solution and add 3 ml of water to the precipitate followed by 9 ml of fuming nitric acid. Chill, centrifuge, and discard the acid. Complete the preliminary separation of the bulk of the calcium by repeating the nitrate precipitation three times, using 5 ml of water and 8 ml of fuming nitric acid for each precipitation.

Strontium and uranium standards are unloaded into 5 ml of strontium carrier solution and the first nitrate precipitation carried out adding 8 ml of fuming nitric acid. The precipitate is dissolved in 5 ml of water and 8 ml of fuming nitric acid added. Repeat the precipitation twice.

After the last fuming nitric acid precipitation, wash the centrifuged strontium nitrate with 5–10 ml of anhydrous industrial methylated spirits. Make the addition quickly with rapid swirling, centrifuge, and discard the alcohol wash. Dissolve the strontium nitrate in 20 ml of water and add 2 ml of 5 *N* hydrochloric acid to make the solution 0.5 *N* in acid. Add 10 mg of antimony carrier and three or four drops of 5 *N* ammonium sulphide reagent. Digest the precipitate in a water bath near the boiling point until it coagulates. Filter, and repeat the scavenge on the filtrate. Test for complete precipitation by adding a drop of sulphide reagent. Discard the precipitates. Add two or three drops of bromothymol blue indicator to the filtrate and then add concentrated ammonia to the neutral point (colour change: yellow to green) followed by six drops in excess. Add 10 mg of cobalt carrier and complete the scavenge as for antimony. Test for complete precipitation of the final cobalt scavenge. Avoid a large excess of ammonium sulphide reagent because it must be destroyed later before attempting the iron hydroxide scavenges.

To the filtrate from the final sulphide scavenge add 0.5 ml of hydrogen peroxide (20 vol) and 5 mg of ferric iron carrier. Insufficient peroxide is indicated by the dark colour of a ferrous sulphide precipitate. If too great an excess of sulphide has been added, a cloud of free sulphur is seen on adding the peroxide. Completion of the oxidation is indicated by the presence of light brown ferric hydroxide. Digest the ferric hydroxide briefly in the water bath. Filter, and repeat the precipitation on the filtrate. Filter while hot and discard the precipitates.

Recover the strontium by heating the solution to 80–90° and adding 10–15 ml of 4 *N* sodium carbonate solution. Digest, centrifuge, and discard the supernatant solution. Wash the precipitate once with water, centrifuge, and discard the washing solution. Add 3 ml of water to the strontium carbonate in the centrifuge tube and run in 9 ml of fuming nitric acid. Chill in an ice bath, centrifuge, and discard the acid. Wash the strontium nitrate with 10–15 ml of anhydrous industrial methylated spirits. Centrifuge and discard the alcohol. Dissolve the nitrate in 2 ml of water and feed to the prepared ion-exchange column (see Experimental Discussion). Rinse the centrifuge tube with 2 ml of water and add to the column as soon as the level of the first 2 ml of solution has dropped to the resin surface. Commence elution with 1 *M* ammonium lactate and 0.05 *M* ammonium citrate as soon as the level of the small volume of wash water falls to the surface of the resin. Collect the eluent in a graduated cylinder. Discard the first nineteen millilitres to pass through the column (calcium is found in the 7–13 ml fraction) and collect the 19–37 ml fraction containing the strontium in another receiver.

Precipitate the strontium with an equal volume (18–20 ml) of saturated ammonium oxalate solution. Permit the slow-forming precipitate to settle before centrifuging. Discard the supernate. Wash the precipitate twice with water, centrifuge, and discard the washings. Dissolve the strontium oxalate in 20 ml of water and a minimum volume (about 1 ml) of 5 *N* hydrochloric acid. Heat to 80–90° in the water bath and very slowly add concentrated ammonium hydroxide dropwise with constant swirling until a permanent precipitate begins to form. Set aside in the water bath to digest for a few minutes and then make ammoniacal. Too rapid addition of ammonia in the second precipitation results in an amorphous precipitate which creeps and is difficult to wash and to slurry evenly on to the counting tray. Cool, centrifuge, and discard the solution. Wash the strontium oxalate twice with 10–15 ml portions of water and twice with similar volumes of anhydrous industrial methylated spirits. Centrifuge each time and discard the washings. Slurry the precipitate with anhydrous alcohol and use a dropping pipette and rubber bulb to transfer the slurry from the centrifuge tube to a weighed beta-counting tray. Tap the tray lightly to settle the precipitate compactly on the bottom of the tray, then dry under an infra-red lamp. Weigh the sources and beta-count.

Correct the observed beta-activity for the background of the counter and, if the range of counts between standards and samples is unduly high, make the appropriate corrections for counter dead-time. Calculate the chemical yield of the source on the basis of the initial quantity of carrier used (60 mg Sr carrier = 132.6 mg of $SrC_2O_4 \cdot H_2O$) and correct the observed activity accordingly. Apply the appropriate factor to correct the beta-count for the self-absorption of the source. Calculate the factor '*f*' for the standards:

$$'f' = \frac{\mu\text{g strontium irradiated}}{\text{corrected activity (c.p.m.)}} = \mu\text{g Sr/c.p.m.}$$

Multiply the corrected activity of the samples by '*f*' to find the weight of strontium originally present in the sample. From this figure and the weight of sample taken, calculate the strontium content.

The strontium-87m activation procedure

Irradiate the samples in either silica phials or polythene ampoules for 2½–3 hours together with strontium standards. Allow the very short-lived activities to decay for two hours before unloading the samples. Dissolve the materials as described in the method for strontium-89 using only 36 mg of strontium carrier, and precipitate the strontium as nitrate. Centrifuge and discard the acid. Dissolve the strontium nitrate in 5 ml of water and add 8 ml of fuming nitric acid. Repeat this precipitation with nitric acid twice (repeat three times for samples like bone ash with a high calcium/strontium ratio). Wash the final precipitate with anhydrous alcohol as already described and dissolve it in 20 ml of water.

Sulphide scavenges are omitted and the two ferric hydroxide scavenges follow immediately upon the last strontium nitrate precipitation. Make the solution slightly ammoniacal and add 5 mg of ferric iron carrier. Digest briefly near the boiling point to aid filtration. Filter, and repeat the hydroxide precipitation with additional iron carrier.

Carefully neutralise the filtrate from the hydroxide scavenges with nitric acid (bromothymol blue indicator). Add to the neutral solution 1 ml of 6 N acetic acid, 2 ml of 6 M ammonium acetate, and 10 mg of barium carrier. Put the centrifuge tube in the water bath and heat almost to boiling. Precipitate barium by the slow addition of 1 ml of 1.5 M sodium chromate reagent. Swirl the contents of the tube constantly as the reagent is added. Digest for a few minutes in the water bath, centrifuge and filter. (The precipitate is finely divided, but does not pass through the filter paper if it is centrifuged before filtration). Repeat the scavenge on the filtrate, adding 10 mg of barium slowly to the hot solution.

Add 2 ml of concentrated ammonium hydroxide to the filtrate from the second barium scavenge. Heat to 80–90° and add 5–10 ml of saturated ammonium oxalate solution. Allow the solution to cool. Centrifuge, and discard the supernate. Wash the precipitated strontium oxalate twice with water, centrifuging each time, and discard the washings. Dissolve the precipitate and reprecipitate it as in the strontium-89 method. Wash twice with water, twice with anhydrous alcohol, and slurry on to a weighed beta-counting tray. Dry under an infra-red lamp, weigh, and beta-count the source. Correct the observed activity for chemical yield (36 mg Sr carrier = 79.6 mg $SrC_2O_4 \cdot H_2O$), self-absorption in the source, and for decay during the counting interval. Compare the corrected activity with that of the standards which have been treated similarly.

Correction factors for absorption and backscatter of radiation from strontium-89 and strontium-87m sources

For the long-lived isotope, irradiate 5–10 mg of strontium (as strontium carbonate, "Specpure") for two weeks in a flux of 10^{12} neutrons/cm^2-sec and allow a cooling period of one week. Dissolve the irradiated strontium in the presence of 60 mg of carrier strontium and pass the strontium through the complex analytical method to ensure radiochemical purity. Before the final oxalate precipitation, add a further 300 mg of strontium carrier and dilute the solution five-fold. Heat the solution to 80–90° and complete the precipitation with 5–10 ml of saturated ammonium oxalate solution and ammonium hydroxide. Centrifuge, wash the oxalate precipitate thoroughly with water and then with anhydrous methylated spirits. Slurry the strontium oxalate on to weighed counting trays endeavouring to produce a series of twelve sources between 30 and 85 mg at intervals of 5 mg. In practice it is simpler to obtain a random distribution of weights. Dry the sources under an infrared lamp, weigh and count. The precipitate can be washed off the trays with alcohol and the sources re-made for a second series of observations.

Correct the observed activity for the background of the beta-counter, and if necessary for the dead-time of the counter. Plot the specific activity (c.p.m./weight in mg) against the source weights as shown in Fig. 2. Draw a smooth curve through the experimental points. In the range between 30 and 50 mg the curve is fairly flat and this value of the specific activity is conveniently taken as the reference value and all others referred to it. Correction factors for selected weights are calculated from the smoothed curve of Fig. 2 and plotted as in Fig. 3. Corrections are almost negligible and need be applied only when particular care is being taken to eliminate all possible sources of error.

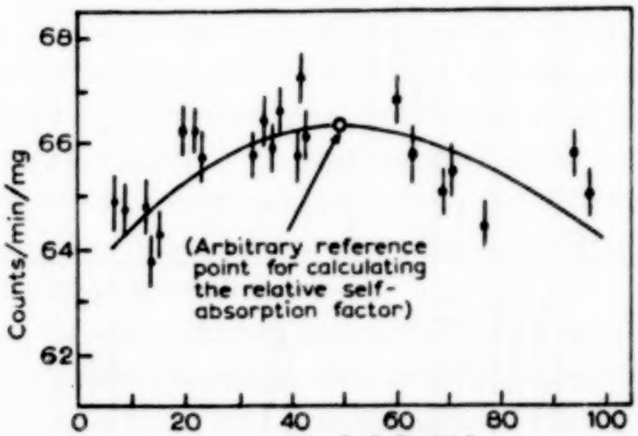

Fig. 2. Variation of specific activity of strontium-89 with source weight.

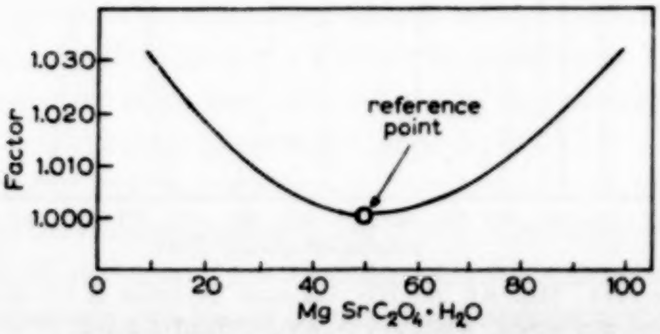

Fig. 3. The relative correction factor for the self-absorption of strontium-89 sources.

For the strontium-87m isotope, no more than 5 mg of strontium need be irradiated for 2½–3 h in order to have ample activity after radiochemical purification (abbreviated method). Add about 200 mg of additional strontium carrier before the final oxalate precipitation, dilute the solution as before and complete the precipitation. After the sources are dried, weigh and count them. Correct the observed activity for decay over the period of counting. Plot the results (see Fig. 4) in the same manner as for strontium-89.

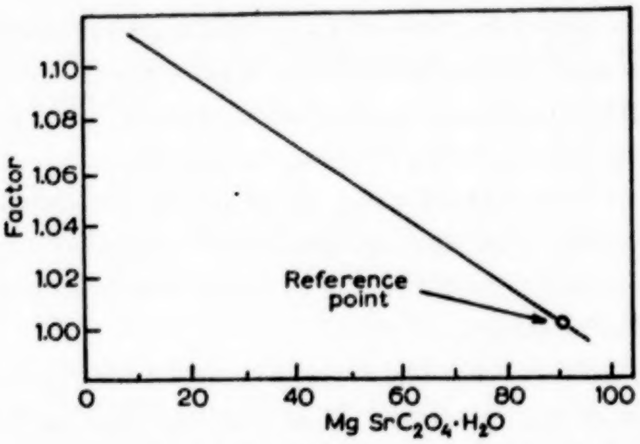

Fig. 4. The relative correction factor for the self-absorption of strontium-87m sources.

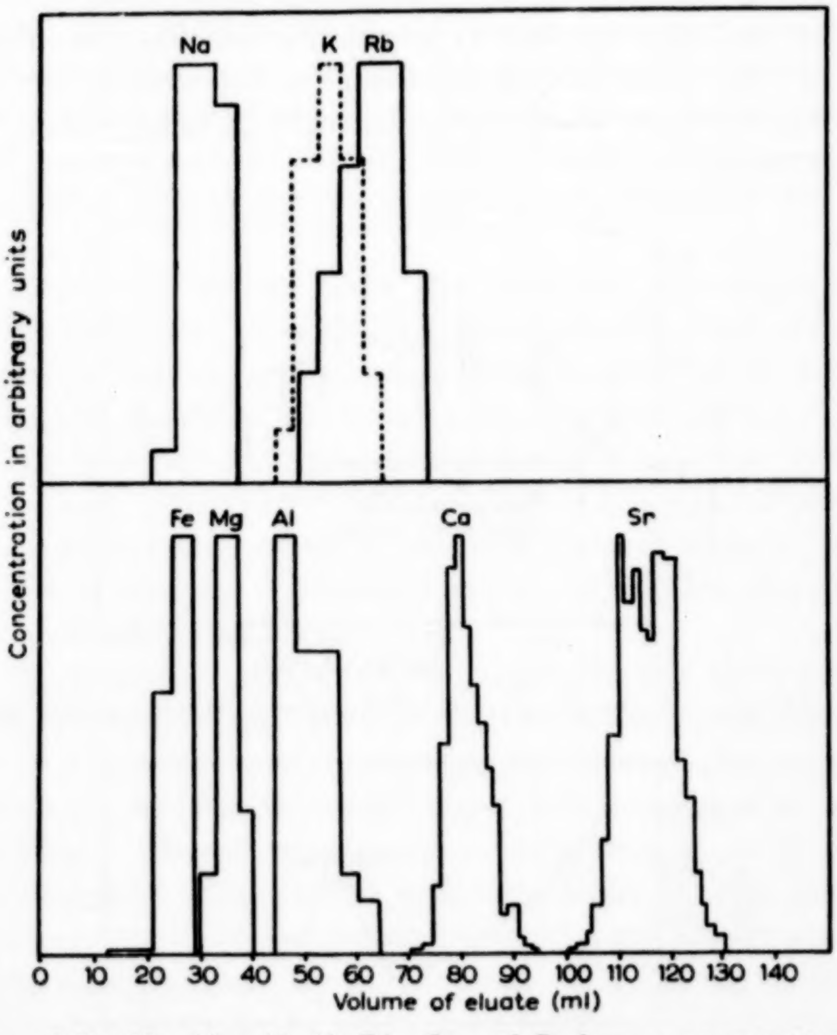

Fig. 5. The elution of Fe, Na, Mg, Al, K, Rb, Ca and Sr from a 12 mm × 210 mm column of Zeo-Karb 225 (15 grams of dry resin) with 2.5 *N* hydrochloric acid. (For clarity the alkali metals are plotted separately from the other elements.)

STABLE ISOTOPE DILUTION ANALYSIS

Experimental discussion

This method requires the addition of a known quantity of enriched strontium-84 tracer to the sample, followed by separation of strontium in a state of purity suitable for a mass spectrometric analysis. Normal strontium (82.5% ^{88}Sr) may then be determined from the difference between the ^{84}Sr/^{88}Sr isotopic ratios of the tracer and of the mixture.

After the addition of tracer the samples were dissolved either in a mixture of hydrofluoric and perchloric acids, or in one of nitric and perchloric acids. Samples of bone ash and soil leachings were first treated with very dilute hydrochloric acid over a period of 1–2 h to avoid losses by spraying. Strontium was then separated by cation-exchange chromatography, the method being very similar to one described by ALDRICH[19]. The sample was placed on a column of Zeo-Karb 225 and eluted with 2.5 N hydrochloric acid. The strontium fraction was evaporated to dryness, again after the addition of nitric acid, and then used in the mass spectrometer. Fig. 5 shows the relative elution positions found for Fe, Na, Mg, Al, K, Rb, Ca and Sr. A mixture of suitable salts of these elements was dissolved in 2.5 N hydrochloric acid, placed on the column, eluted, and 36 fractions of 3–4 ml collected. The first six of these elements were located by emission spectroscopy; these analyses were kindly made by Mr. F. T. BIRKS, Analytical Chemistry Branch, Harwell. Calcium and strontium were located with radioactive tracers.

ALDRICH[20] stated that some of the aluminium was often present in the strontium fraction, so the elution position of this element was checked under a variety of conditions. In each case about 100 mg of aluminium was placed on the column, eluted, and located in the fractions by precipitation with ammonia. Provided an aluminium salt was merely dissolved in hydrochloric acid and then eluted from the column the elution position found was similar to that shown in Fig. 5. If the aluminium salt was first treated with a mixture of hydrofluoric and perchloric acids, either alone or mixed with granite (G–1), it was eluted from the column by a smaller volume, usually appearing in the fraction 15–25 ml, presumably because of the formation of a fluoride complex. The elution position of strontium was also determined under various conditions, but no significant variation was found.

It must be emphasized that the elution curve shown in Fig. 5 shows only the *relative* elution positions of the various elements. The absolute positions may vary between apparently similar batches of resin and it is essential to make an investigation with radioactive strontium tracer for each batch. For example in one case, after the columns had been refilled with fresh resin, strontium required a smaller volume of acid for complete elution, and if the fraction collected had been based on the initial calibration it could have contained as little as 0.1 – 1% of the strontium. Under these conditions any contamination acquired after the ion-exchange stage would have a disproportionately large effect and could cause extremely large errors.

For samples containing high strontium concentrations it was possible to make a determination without an ion-exchange separation. The sample and tracer were merely dissolved in nitric acid and a portion used directly for a mass spectrometric analysis. Large rubidium beams were produced in the mass spectrometer, but by heating the sample on the filament overnight, rubidium could be evaporated from the sample and the rubidium ion beam intensity reduced to a negligible level; an analysis could then be made for strontium. Results obtained in this way were of poor precision but agreed well with later determinations made with a separation. Table V records these analyses and also the mean values and standard deviations of later determinations made with a separation. In the case of sample 7 this direct analysis for strontium was made in the presence of a 400-fold excess of calcium.

TABLE V

DETERMINATIONS OF STRONTIUM IN SOIL LEACHINGS MADE BOTH DIRECTLY AND AFTER AN ION-EXCHANGE SEPARATION

Sample	*Direct determinations p.p.m.*		*Comparison determinations p.p.m.*
Soil leachings (West Virginia) (Sample No. 7)	610 620 660	630	616.5 ± 1.2
Soil leachings (Mississippi) (Sample No. 8)	2890 2940 3150	2990	2973 ± 38

Isotopic analyses were made with a 6″ radius of curvature 60° sector mass spectrometer containing a surface ionisation source and the conventional detector system of a Type 954 electrometer valve and a dc-amplifier. The measured $^{84}\mathrm{Sr}/^{88}\mathrm{Sr}$ isotopic ratios were used to calculate the quantity of strontium in a sample with the following equation:

$$x = y \cdot \frac{R_{\mathrm{T}} - R_{\mathrm{M}}}{R_{\mathrm{M}} - R_{\mathrm{N}}} \cdot \frac{84R_{\mathrm{N}_4} + 86R_{\mathrm{N}_6} + 87R_{\mathrm{N}_7} + 88}{84R_{\mathrm{T}_4} + 86R_{\mathrm{T}_6} + 87R_{\mathrm{T}_7} + 88}$$

where: x = the mass of strontium present in the sample; y = the mass of strontium tracer added; R_{M} = the $^{84}\mathrm{Sr}/^{88}\mathrm{Sr}$ isotope ratio for the mixture; R_{N} = $^{84}\mathrm{Sr}/^{88}\mathrm{Sr}$ isotope ratio of normal strontium; R_{T} = the $^{84}\mathrm{Sr}/^{88}\mathrm{Sr}$ isotope ratio of tracer strontium; R_{N_4} = the $^{84}\mathrm{Sr}/^{88}\mathrm{Sr}$ isotope ratio of normal strontium; R_{N_6} = the $^{86}\mathrm{Sr}/^{88}\mathrm{Sr}$ isotope ratio of normal strontium, etc.

The strontium-84 tracer had the following measured isotopic composition: $^{84}\mathrm{Sr}$ 50.5%, $^{86}\mathrm{Sr}$ 12.0%, $^{87}\mathrm{Sr}$ 3.6%, $^{88}\mathrm{Sr}$ 33.9%. The concentration of a solution of this tracer was determined by isotope dilution with a standard prepared from Johnson Matthey's "Specpure" strontium carbonate. About 1 g of strontium carbonate was dried at 180° for 24 h and used to prepare a solution of accurately known concentration of about 10 μg/ml. Aliquots of this dilute standard were added to aliquots of the tracer and the $^{84}\mathrm{Sr}/^{88}\mathrm{Sr}$ ratios of the mixtures determined. The coefficient of variation for five determinations of the concentration was 1.5%.

Blank corrections were determined by processing a portion of the tracer under the same conditions as those used for the samples. A blank correction was not usually greater than 0.3 μg. It never represented more than 4% of the quantity of strontium determined, and the average blank correction was about 1%. Hydrochloric acid was purified by distillation in quartz apparatus, and water by mixed bed ion exchange. Otherwise AnalaR grade reagents were used. All evaporations were made under glass or silica covers. Solutions came into contact only with platinum, silica or polythene.

The cation-exchange columns were washed with 300 ml of 2.5 N hydrochloric acid before each series of determinations.

ANALYTICAL METHOD

Preparation of cation-exchange columns

The resin used is Zeo-Karb 225, particle size 50 μ diameter, supplied by "The Permutit Company Ltd". Place 2 lb of resin in a suitable tube and wash with $\sim$20 l of 2.5 N hydrochloric acid. Wash the resin thoroughly with water, and then spread out on filter paper to dry for several days. When dry, store in a polythene bottle and mix thoroughly. This provides sufficient dry resin for about thirty columns.

Weigh out 15 g of resin and transfer as a slurry into a column. A piece of $\frac{1}{2}''$ polythene tube 10–12″ long fitted with a silica tip forms a suitable container. The resin is retained with a plug of cotton wool at each end. Wash the column with 300 ml of 2.5 N hydrochloric acid before each determination.

Determine the elution position for strontium with one column. Place an aliquot of strontium-89 tracer on the column and elute with 2.5 N hydrochloric acid. Discard the first 60 ml of eluate and then collect 3–5 ml fractions. To each fraction add 10 mg of strontium carrier, neutralise with ammonia and add excess sodium carbonate reagent. Wash the precipitate first with water and then with industrial methylated spirits, and transfer as a slurry in industrial methylated spirits on to an aluminium tray for beta-counting.

TABLE VI

THE STRONTIUM CONTENT IN p.p.m. OF EIGHT INTERNATIONAL SAMPLES OF BIOCHEMICAL INTEREST DETERMINED BY NEUTRON ACTIVATION AND STABLE ISOTOPE DILUTION, TOGETHER WITH COMPARATIVE SPECTROGRAPHIC RESULTS

Sample No.	*Material*	*Neutron activation results*		*Isotope dilution results*		*Spectrographic results*
		strontium-89 method	*strontium-87m method*			
1	Alfalfa	124	128	118 120 126	121.5 ± 5	120, 100, 100
2	Clover and rye grass	64	68	64 67	65 ± 2	55
3	Milk powder (Utah)	8 ± 1	7 ± 1	7.3 7.3 7.8	7.5 ± 0.3	7 ± 1
4	Milk powder (Italy)	8 ± 1	6 ± 1	5.8 6.2 6.4	6.2 ± 0.4	7 ± 1
5	Bone ash (Baltimore, N.J.)	310	306	293 314 325	311 ± 17	240
6	Bone ash (Camden, N.J.)	445	431	427 428 440	432 ± 10	300
7	Soil leachings (West Virginia)	658	656	615.5 616.5 618	617 ± 9	880, 710, 890
8	Soil leachings (Mississippi)	3000	2980	2930 2980 3010	2975 ± 60	3500

Treatment of samples

Weigh out a suitable aliquot of strontium-84 tracer in a platinum dish and evaporate to dryness. Weigh out the sample and decompose with hydrofluoric and perchloric acids, or with nitric and perchloric acids. Dissolve the residue in 3 ml of 2.5 *N* hydrochloric acid and place on a column. Wash with 1–2 ml of water and then elute with 2.5 *N* hydrochloric acid. Collect the strontium fraction in a polythene bottle and evaporate to dryness in the original platinum dish. Heat to redness to decompose organic material. Add a few ml of nitric acid and evaporate to dryness. Dissolve the residue in one drop of demineralised water and transfer to the filament of a mass spectrometer source unit.

RESULTS AND DISCUSSION

The results of strontium analyses by neutron activation and isotope dilution on

TABLE VII

THE STRONTIUM CONTENT IN p.p.m. OF TWO STANDARD ROCK SAMPLES, TWO MISCELLANEOUS SAMPLES OF BONE ASH AND FOUR OF SODIUM SULPHATE

(The precision of the neutron activation figures is estimated to be about ±3%)

Material	*Neutron activation strontium-89 method*	*Stable isotope dilution*	*Comparative analyses*[a]
Granite, G-1	252[b]	224 238 240 241 } 236 ± 9	233 I.D., Herzog[7] 262 I.D., Turekian[8] 287 E.S., Turekian[8] 120 E.S., Murata[8] 220 E.S., Harvey[8] 250 E.S., Ahrens[8] 280 E.S., Nockolds[8] 900 E.S., Mitchell[8]
Diabase, W-1	172[b]	177 177 181 184 } 180 ± 4	177 I.D., Herzog[7] 178 I.D., Turekian[8] 172 E.S., Turekian[8] 120 E.S., Murata[8] 180 E.S., Harvey[8] 180 E.S., Nockolds[8] 250 E.S., Ahrens[8] 420 E.S., Mitchell[8]
Bone ash No. 37 (from Dr. S. R. Stitch)	143	—	144 N.A., Sowden and Stitch[2]
Bone ash No. 38 (from Dr. S. R. Stitch)	136	—	146 N.A., Sowden and Stitch[2]
Sodium sulphate I	12	—	
II	41	41.6 42.3 } 42 ± 2	
III	13	—	Sample supplied as a test. Believed to be 2 p.p.m. in Sr, spiked with a further 10 p.p.m.
IV	58	51	

[a] I.D. = Isotope dilution. E.S. = Emission spectroscopy. N.A. = Neutron activation.
[b] Corrected for presence of uranium.

TABLE VIII

THE STRONTIUM CONTENTS OF SAMPLES FROM THE SKAERGAARD INTRUSION, EAST GREENLAND

Sample	*Uranium content p.p.m. and method of determination*	*Strontium content p.p.m. calculated from total Sr radioactivity*	*Correction for uranium (p.p.m. Sr)*	*Strontium content corrected mean value p.p.m.*
E.G. 1851 Perpendicular Feldspar Rock	0.3 Estimated	244 246 250 249	—2	245
E.G. 4328 Upper Ferrogabbro	0.4–0.5 Fluorimetry	188 187 196 193	—4	187
E.G. 4329 Upper Ferrogabbro	0.4 Estimated	221 217 224 221	—4	217
E.G. 4330 Fayalite Ferrogabbro	2 Estimated	457 453 464 464	—18	442
E.G. 4332 Hedenbergite Granophyre	1.1 Radioactivation	255 256 248 252	—7	246
E.G. 4427 Middle Gabbro	0.27 Fluorimetry	177 175 171 169	—2	171
E.G. 4489 Transgressive Granophyre Sill	3.5 Radioactivation	336 326 319 332 333	—23	306
E.G. 4507 Chilled Marginal Gabbro	0.2 Radioactivation	268 268 269	—1	267
E.G. 4526 Gabbro Picrite	0.07 Radioactivation	112 116 114 115	—	114
E.G. 5181 Lower Ferrogabbro	0.1 Fluorimetry	309 317 298 313	—1	308

eight international samples of biochemical interest are given in Table VI. Almost a year elapsed between the series of analyses employing the strontium-89 isotope and those using the strontium-87m method. Replicate neutron activation analyses lead to an estimated precision of 3% with the exception of the results on milk powders where the uncertainty is higher because the quantity of strontium is close to the lower limit of the procedure. The uncertainty quoted for each result obtained by stable isotope dilution analysis represents the overall standard deviation for the set of determinations and for the calibration of the strontium-84 tracer. The last column of Table VI shows the independent spectrographic analyses submitted by Mr. F. W. J. GARTON (U.K.A.E.A., Woolwich Outstation).

Omitting the results on milk powders, the average agreement between the two neutron activation methods is ±2% of the mean. Bearing in mind the estimated precision of 3%, neither method appears to suffer from an inherent bias. The figures obtained by stable isotope dilution and neutron activation are in satisfactory agreement, with the possible exception of the sample of West Virginia Soil Leachings. The spectrographic figures also agree within the estimated accuracy of the data (±20%) with the results obtained by the other methods on the first four samples in Table VI. The spectrographic results are notably lower for the bone ash and higher for the soil leachings than the figures obtained by neutron activation and isotope dilution.

Table VII sets out comparative analytical results for two samples of bone ash (supplied by Dr. S. R. STITCH, Radiobiological Unit, Medical Research Council, A.E.R.E.), four samples of sodium sulphate, and samples of standard granite, G-1, and standard diabase, W-1.

Table VIII reports a series of neutron activation analyses for the strontium content of certain rocks from the East Greenland Skaergaard intrusion. These samples were kindly supplied by Prof. L. R. WAGER and Dr. E. A. VINCENT of the Department of Geology and Mineralogy, University of Oxford. A uranium standard was irradiated with each of these samples and a correction for fission product strontium applied to the sample analyses in proportion to their uranium content. The figures for the uranium content were obtained from either fluorimetric or neutron activation analyses or, where no analyses were available, from estimates based upon analyses of other comparable rocks. The average correction was 3%.

SUMMARY

Methods are described for the determination of strontium in a variety of materials by neutron activation and by stable isotope dilution. The samples for neutron activation analysis, together with strontium standards, are irradiated in a high neutron flux for a few hours (strontium-87m, 2.7 hour half-life) or for a week or more (strontium-89, 54 day half-life). After dissolving in the presence of strontium carrier, samples and standards are subjected to radiochemical purification. The beta activity induced in the samples and standards is compared and the quantity of strontium in the sample calculated by proportion. Somewhat less than one microgram of strontium can be determined. For stable isotope dilution analysis, the sample is mixed with a known quantity of strontium-84 tracer and dissolved in a mixture of hydrofluoric and perchloric, or nitric and perchloric acids. Strontium is then usually separated by cation-exchange chromatography it is possible to obtain spectrometric analysis, but for samples with large strontium concentrations before making the mass results without a separation. The main source of systematic error is strontium contamination, but with simple precautions this may be restricted to 1–4% of the quantity of strontium determined and a correction applied.

RÉSUMÉ

Des méthodes radiochemiques sont décrites pour le dosage du strontium, soit par activation au moyen de neutrons, soit par dilution isotopique. Pour l'analyse par activation, on irradie dans un flux de neutrons simultanément l'échantillon à analyser et un strontium étalon; on compare les activités bêta et on peut alors calculer la teneur en strontium de l'échantillon. Pour l'analyse par dilution isotopique, l'échantillon est mélangé avec un traceur (strontium-84) et dissous dans un mélange d'acides. Le strontium peut être ensuite séparé par chromatographie avant de procéder à l'analyse spectrométrique de masse.

ZUSAMMENFASSUNG

Beschreibung radiochemischer Methoden zur Bestimmung von Strontium durch Aktivierung mit Neutronen oder nach der Isotopen-Verdünnungsmethode. Bei dem Aktivierungsverfahren wird eine Strontiumprobe als Vergleichssubstanz mit-bestrahlt. Durch Vergleich der Aktivitäten lässt sich der Strontiumgehalt berechnen. Bei der Isotopen-Verdünnungsmethode wird die Substanz mit Strontium-84 als Tracer gemischt, das Strontium über einen Jonenaustauscher abgetrennt und anschliessend massenspektrometrisch bestimmt.

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EFFECT OF ABSORBANCY UPON RAMAN INTENSITIES IN LIQUIDS

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In recent studies carried out by the author on the Raman effect in liquid an extremely noticeable effect upon Raman intensities was observed which was directly correlated to the absorbancy of the materials being studied. Placzek[1] and several recent authors[2,3] have considered the alteration in Raman intensity as the exciting line enters an absorption band. It is stated that the intensity rises due to a resonance phenomenon which results in an increase in the transition probability. In addition to the resonance phenomenon encountered it is also felt in the light of recent studies[4] that the absorbancy of the material in question quite frequently plays a deciding factor in the resultant Raman intensity. Consequently it was felt desirable to apply absorbancy laws to the Raman process. In particular the physical circumstance of peripheral illumination by means of a helical lamp upon a Wood's model Raman tube was considered[5].

Raman excitation of a liquid can be visualized as occurring in three steps: light traverses the solution, interacts with the solution producing Raman radiation, and then traverses the solution until it is collected at the monochromator slit. For the particular case of illumination of a Wood's tube we may consider that illumination by a helical lamp can be pictured as illumination by a cylinder of light. The light from a given cross section of the Raman tube then passes the length of the tube and is gathered by a suitable lens. For a given cross section of the tube light must travel a path r, see Fig. 1, to the point of excitation O. The excitation intensity at O is given by the Lambert-Beer law:

$$I_1/I_0 = \mathrm{e}^{-a_1 cr(\theta)}$$

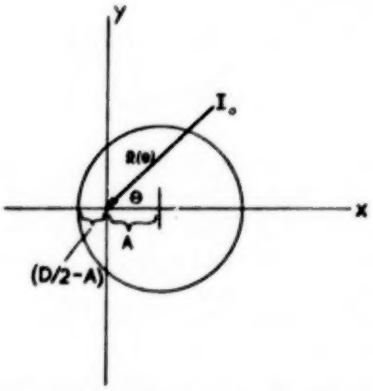

Fig. 1. Cross section of the Raman tube.

where I_1 and I_0 are respectively the final and initial intensity; a, the absorbancy coefficient for the Raman excitation line; c, the concentration of solute; and $r(\theta)$, the distance r as a function of radial angle of illumination. If now we consider the full range of r and integrate the intensity over the whole cross section of the tube we find the illumination intensity at a given cross section is:

$$I_1/I_0 = \frac{4\pi}{a_1^2 c_1^2} \left(1 + \mathrm{e}^{-a_1 c_1 D} - 2\,\mathrm{e}^{-a_1 c_1 D/2}\right)$$

where D is the diameter of the tube. The contribution of axial illumination is not considered in this expression as its contribution is small relative to radial illumination. The material at a given point of illumination may scatter by either a Raman or Rayleigh process. The former process may be represented as:

$$I_2/I_1 = K_1 c_1$$

where K_1 is the transition probability of the Raman process, and c_1 is the concentration of specie undergoing excitation. The Rayleigh scattering process may originate from either the solvent or solute; thus for the Rayleigh process we have:

$$I_2/I_1 = K_{\mathrm{solvent}}\, c_{\mathrm{solvent}} + K_{\mathrm{solute}}\, c_{\mathrm{solute}}$$

The light reaching the condensing lens must travel a path along the length of the tube from the point of excitation. In most liquids the case of back scattering is negligible and will not be considered. The total intensity at the face of the Wood's tube is given by the integration of light intensity over the length of the tube L:

$$I_f/I_2 = 1/a_2 c_1 \left(1 - \mathrm{e}^{-a_2 L c_1}\right)$$

where a_2 is the absorbancy coefficient for the Raman line. The complete process for

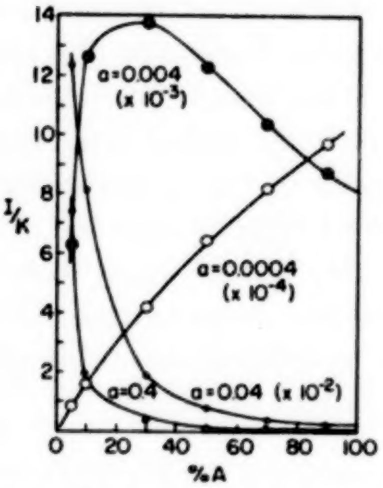

Fig. 2. Calculated intensity for variation in a ($a_{11} = a_{12}$), $D = 5.1$ cm, $L = 20.3$ cm.

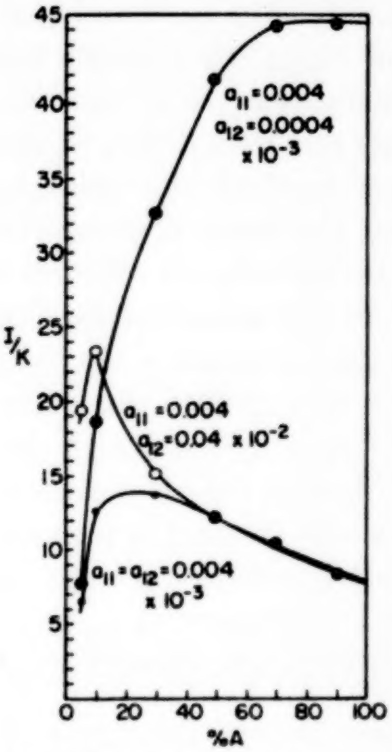

Fig. 3. Calculated intensity for variation in a_{11}, a_{12}, $D = 5.1$ cm, $L = 20.3$ cm.

Raman scattering is thus given by:

$$I_1/I_0 \cdot I_2/I_1 \cdot I_1/I_2 = I_f/I_0$$

or:

$$I_f/I_0 = \frac{4\pi}{a_1^2 c_1^2} \left[e^{-a_1 c_1 D} + 1 - 2\, e^{-a_1 c_1 D/2}\right] \left[K_1 c_2\right] \left[1/a_2 c_1 \left(1 - e^{-a_1 L c_1}\right)\right]$$

For the Rayleigh scattering process the $K_1 c_1$ term is substituted by:

$$\Sigma K_1' c_1'$$

i.e. the summation of scattering from all components present. The variation in intensity with concentration as effected by the parameters is shown in Figs. 2 through

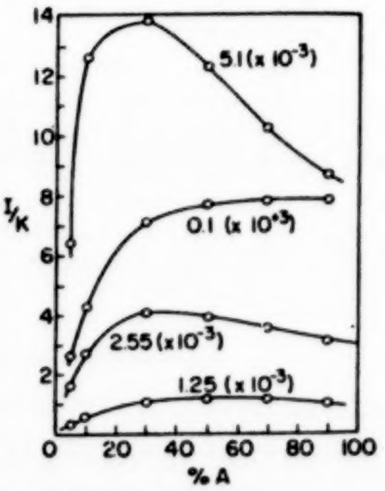

Fig. 4. Calculated intensity for variation in D, $a = 0.004$, $L = 20.0$ cm.

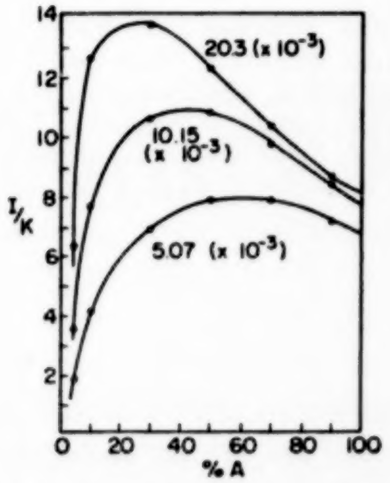

Fig. 5. Calculated intensity for variation in L, $a = 0.004$, $D = 5.1$ cm.

5. In Fig. 2 it is to be noted that there is a general trend of increasing intensity for decreasing absorbancy coefficient also we see that for high absorbancy coefficient the intensity rises to a maximum, the more abruptly the larger the absorbancy coefficient, and then drops, again the more abruptly the larger the coefficient. As the absorbancy coefficient diminishes the trend is reversed until at low absorbancy coefficient, the trend is completely increasing with concentration. Fig. 3 shows the effect of independently altering a_1 and a_2. Fig. 4 shows the effect produced on the intensity by alteration of the diameter of the Wood's tube. For large diameter the intensity goes through a maximum and then declines. This maximum becomes less prominent the smaller the diameter of the tube. It is to be noted that the total intensity falls in general with decreasing diameter. Finally in Fig. 5 the variation in length of Wood's tube is considered. For greatest length of Wood's tube the intensity again proceeds through a maximum and then declines. With decreasing tube length the overall intensity fall and the maximum becomes less pronounced. Thus the absorbancy coefficient of a given material may be seen to indicate desirable physical sizes of equipment as well as preferable concentration ranges for study.

ACKNOWLEDGEMENT

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SUMMARY

An equation is proposed relating Raman intensity of liquids to the absorbancy of the liquid and geometric factors in the design of the Raman tube. Calculations are carried out which show the effect of concentration on intensity for variation in absorbancy, length and diameter of Raman tube.

RÉSUMÉ

Une équation est proposée, montrant la relation entre l'intensité Raman dans les liquides et leur absorption, ainsi que les dimensions du tube Raman (longueur, diamètre).

ZUSAMMENFASSUNG

Die Beziehungen zwischen Raman Intensität, und Absorptionsfähigkeit von Flüssigkeiten sowie der Einfluss der geometrischen Faktoren der Raman Röhren werden durch eine Gleichung ausgedrückt.

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SPECTROPHOTOMETRIC DETERMINATION OF TELLURIUM(IV) WITH 1,1'-DIANTHRIMIDE

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INTRODUCTION

The organic reagent 1,1'-dianthrimide is normally applied for spectrophotometric determination of small amounts of boron. In an earlier publication[1] the photometric determination of germanium with 1,1'-dianthrimide was described; in the present paper the determination of tellurium with 1,1'-dianthrimide is proposed. The reactions of boron, germanium and tellurium with 1,1'-dianthrimide take place in concentrated sulphuric acid, the colours of the complexes being developed by heating.

No reference is made in the literature to the use of 1,1'-dianthrimide for the detection or determination of tellurium.

INSTRUMENTS AND REAGENTS

Instruments

Extinction measurements were made with a Zeiss spectrophotometer PMQ II, 0.5-cm glass cells being used.

Reagents

The spectrographically standardized tellurium dioxide (Johnson, Matthey & Co.) contained the following amounts of impurities: 2 p.p.m. tin; 1 p.p.m. copper, iron, lead, magnesium, silicon and sodium; and less than 1 p.p.m. calcium, manganese and silver. Concentrated sulphuric acid (95–97%) and other chemicals (including 1,1'-dianthrimide) were of reagent grade quality. The strength of the stock solution of sulphuric acid was determined volumetrically and found to be 96.12%. Ordinary distilled water from an all-metal still was used. The solutions were prepared and heated in 50-ml bottles (Jena Geräteglass) with ground glass stoppers. The solutions were heated in a thermostatically controlled drying oven of standard construction.

Standard solutions

Tellurium dioxide (62.5 mg) was dissolved in some ml of 1% sodium hydroxide solution. After dilution to 50 ml with 1% sodium hydroxide solution, the standard solution was stored in a plastic bottle. This solution contained 1 mg of tellurium per ml. A 1% solution of sodium hydroxide served as blank. 1,1'-Dianthrimide (1.250 g) was dissolved in 96.12% sulphuric acid, and the solution was diluted to 250 ml with the same acid. The solution contained 5 mg of 1,1'-dianthrimide per ml.

EXPERIMENTAL

Absorption curves

The absorption curve of a 10^{-4} *M* solution of 1,1'-dianthrimide in concentrated sulphuric acid gave (when measured against concentrated sulphuric acid) small and nearly constant extinction values in the range 500 to 700 mμ. At lower wavelengths the extinction increased rapidly, and at higher wavelengths the extinction decreased.

In more concentrated solutions (about 10^{-3} M) of 1,1'-dianthrimide a broad absorption band appeared at about 650 mμ; in more dilute solutions (about 10^{-5} M) a maximum was observed at about 350 mμ.

The complex between tellurium and 1,1'-dianthrimide showed two absorption maxima at 550 and 600 mμ. (The absorption maxima of the boron 1,1'-dianthrimide and the germanium 1,1'-dianthrimide complexes are found at about 630 and 660 mμ, respectively).

Effect of concentration of sulphuric acid

Before testing the validity of the Lambert-Beer law, the effect of concentration of sulphuric acid on the development of the colour was investigated for solutions heated for 16 h at 70°.

A series of solutions was prepared in which the concentrations of tellurium and 1,1'-dianthrimide were kept constant, while the concentration of sulphuric acid was varied. 0.2 ml of the tellurium standard solution, 20 ml of the different sulphuric acids and 5 ml of the 1,1'-dianthrimide solution were pipetted into 50-ml bottles. The series of blank solutions prepared contained 0.2 ml of 1% sodium hydroxide solution, 20 ml of sulphuric acid and 5 ml of 1,1'-dianthrimide standard solution. After heating, the extinctions of the sample solutions were measured against the corresponding blanks at the wavelength of the absorption maximum 600 mμ. The data obtained are given in Table I.

TABLE I

EFFECT OF CONCENTRATION OF SULPHURIC ACID ON THE DEVELOPMENT OF THE COLOUR OF THE TELLURIUM 1,1'-DIANTHRIMIDE COMPLEX

Concn. (in per cent) of the sulphuric acid added	82.67	86.38	92.78	96.12	97.85	98.75	99.45
Extinctions at 600 mμ	0.066	0.126	0.230	0.310	0.336	0.334	0.212

It is seen from Table I that the strength of sulphuric acid was not critical when the concentration of the 20 ml of acid added was within the range 96.12 to 98.75%. Above and below this range lower extinction data were obtained.

Calibration curve

On the basis of the above results a calibration curve was plotted for a series of solutions containing 20 ml of 97.85% sulphuric acid. Into 50-ml bottles were pipetted 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 ml of tellurium standard solution. Volumes of less than 0.6 ml were diluted to that volume with 1% sodium hydroxide solution. Then 20 ml of 97.85% sulphuric acid and 5 ml of 1,1'-dianthrimide standard solution were added. The blank solution consisted of 0.6 ml of 1% sodium hydroxide solution, 20 ml of 97.85% sulphuric acid and 5 ml of 1,1'-dianthrimide standard solution. After 16 h of heating at 70° the extinctions of the sample solutions were measured against the blank at 600 mμ. The data obtained are given in Table II.

It is seen from Table II that a negative deviation from the Lambert-Beer law was obtained within the concentration range examined.

TABLE II

CALIBRATION CURVE FOR THE DETERMINATION OF TELLURIUM WITH 1,1'-DIANTHRIMIDE

Mg tellurium taken (A)	*Extinction (E)*	*Extinction index (E/A)*
0.1	0.168	1.68
0.2	0.332	1.66
0.3	0.470	1.57
0.4	0.588	1.47
0.5	0.700	1.40
0.6	0.840	1.40

Effect of temperature

In concentrated sulphuric acid tellurium and 1,1'-dianthrimide react very slowly. The rate of reaction increases with temperature, but even at 70° the colour development was quite slow.

On the basis of unpublished results from an investigation of the boron 1,1'-dianthrimide complex, it is possible to indicate the effect of higher heating temperatures. When solutions of boron and the reagent were heated at 80° or higher, the extinctions decreased compared with solutions heated at 70°. At higher temperatures a red colour appeared in addition to the colour of the complex, the red colour probably originating from a decomposition product of 1,1'-dianthrimide. Consequently, a heating temperature above 70° cannot be recommended for the formation of the tellurium 1,1'-dianthrimide complex.

Effect of heating time

A relatively long heating time was necessary to obtain equilibrium conditions. The solutions were heated for 16 h at 70°; a longer time caused a decreased extinction, probably again owing to decomposition of the complex.

Influence of foreign ions

On the basis of an investigation of the ions interfering in the determination of boron with 1,1'-dianthrimide, it is possible to obtain information about the ions interfering in the determination of tellurium. The following ions interfere: boron, germanium(IV), bromide (oxidized in concentrated sulphuric acid) and fluoride. The interference of fluoride is probably due to attack on glass and release of boron.

SUMMARY

Tellurium and 1,1'-dianthrimide form a coloured complex with absorption maxima at 550 and 600 mμ, which can be used spectrophotometrically. Boron and germanium are known to react similarly; bromide and fluoride interfere.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage du tellure au moyen de dianthrimide-1,1'. Ce réactif réagit également avec le bore et le germanium. La réaction est perturbée par les anions Br^- et F^-.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Bestimmung von Tellur mit Dianthrimid-1,1' beschrieben. Bor, Germanium, Brom und Fluor stören.

REFERENCE

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SIMULTANEOUS DETERMINATION OF SILICON AND PHOSPHORUS IN THE PRESENCE OF EACH OTHER

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The most widely used method for the determination of silicon and phosphorus is the spectrophotometric method. This involves the formation of the yellow silicomolybdate and phosphomolybdate, followed by reduction of these complexes to molybdenum blue.

During the investigation leading to the colorimetric determination of silicon in the presence of phosphorus, PAUL AND POVER[1] reported the separation of silicomolybdate from phosphomolybdate by selective extraction of the latter with ethyl acetate. Reduction of the silicomolybdate in the aqueous phase provided an accurate and reliable method for determination of silicon in the presence of phosphorus.

The possibility of simultaneously determining phosphorus in the solvent phase was considered. De SESA AND ROGERS[2] have reported the simultaneous determination of silicon and phosphorus by measurement of the total absorbance of the yellow molybdate at 332 mμ, extraction of the phosphomolybdate with isoamyl acetate and measuring the absorbance of the organic phase at 330 mμ. Correction of the total absorbance in the aqueous phase for phosphorus, using the previously determined absorbance index of phosphomolybdate, gave the silicon content.

This technique though feasible was time-consuming. However, while investigating the solvent extraction technique, a spectrophotometric method was developed for the simultaneous determination of silicon and phosphorus as molybdenum blue.

This paper reports the investigations leading to this method and the tests conducted on the procedure.

EXPERIMENTAL

Reagents

All reagents were of AnalaR grade. Distilled water was used throughout.

Silicate solutions: Solutions of soluble silica were prepared by fusing 10.0 mg of finely divided quartz with 0.5 g of powdered sucrose and 1.5 g of sodium peroxide in a Parr-bomb, and dissolving the melt in 100 ml water in a polythene beaker. Further solutions of silicate were prepared by dilution.

Phosphate solutions: A stock solution of phosphorus was prepared by dissolving 0.50 g of sodium dihydrogen phosphate (dihydrate) and diluting to 100 ml. Further solutions of phosphate were prepared from it by dilution.

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Amino-naphthol-sulphonic acid reagent: 0.20 g of 1-amino-2-naphthol-4-sulphonic acid, 2.4 g sodium sulphite ($7H_2O$) and 12.0 g sodium metabisulphite dissolved in water and made up to 100 ml. The reagent was kept in a dark bottle and freshly prepared weekly.

Silicon and phosphorus determination

Silicon and phosphorus were determined by the same colorimetric method. This involved the formation of yellow molybdates of silicon and phosphorus, and their reduction to the corresponding heteropoly blue with 1-amino-2-naphthol-4-sulphonic acid reagent. The silico-heteropoly blue was measured at 690 mμ and the phospho-heteropoly blue at 660 mμ. The reagents which were found to give accurate and reproducible results for both silicon and phosphorus determination are given in the order in which they were added:

2.0 ml silicate (60 to 10 μg) or phosphate (50 to 400 μg), 2.0 ml hydrochloric acid (*N*), 1.0 ml perchloric acid (72%), 4.0 ml ammonium molybdate solution (5%), 0.5 ml 1-amino-2-naphthol-4-sulphonic acid reagent.

Blanks made with 2 ml distilled water and the standard reagents, were used to set the colorimeter to read 100% transmission before the optical density of the test material was measured.

PROCEDURE FOR SIMULTANEOUS DETERMINATION OF SILICON AND PHOSPHORUS

2.0 ml of the test solution were pipetted into a 50-ml separating funnel, followed by 2.0 ml hydrochloric acid. 1.0 ml perchloric acid was then added and the solution shaken for about 1 min. 4.0 ml ammonium molybdate solution were added and the solution mixed by shaking for about 3 min, after which 0.5 ml of 1-amino-2-naphthol-4-sulphonic acid reagent was added with continuous shaking. The resulting solution was allowed to stand for 10 min for maximum colour to develop. The contents of the separating funnel were then extracted with 20.0 ml of diethyl ether for 30 sec. The aqueous phase was separated and its optical density measured immediately at 690 mμ against a similarly treated blank. The colour of the organic phase was measured at 660 mμ against a solvent blank.

RESULTS

In Table I is recorded the extraction of phospho- and silico-heteropoly blue by various solvents. 98.3% of the phospho-heteropoly blue was extracted by *n*-propyl acetate,

TABLE I

SOLVENT EXTRACTION OF HETEROPOLY BLUE OF PHOSPHORUS AND SILICON

Solvent	*Phosphate found in solvent phase after extraction of phosphate blue*[a] *μg*	*Silica found in aqueous phase after extraction of silicate blue*[b] *μg*
ethyl acetate	300	50
n-propyl acetate	295	52
isopropyl acetate	295	52
n-butyl acetate	—	53
isobutyl acetate	294	56
isoamyl acetate	235	60
diethyl ether	295	59
chloroform	<5	60
tetrachloroethane	<5	60
carbon tetrachloride	<5	60
benzene	<5	60
petroleum ether (b.p. 40–60°)	<5	60

[a] Initial phosphate concentration 300 μg/2 ml.

[b] Initial silicate concentration 60 μg/2 ml.

isopropyl acetate, isobutyl acetate and diethyl ether. Isoamyl acetate extracted the phospho-heteropoly blue to the extent of 79.3% while ethyl acetate was 100% efficient. *n*-Amyl acetate and dibutyl ether were found to bleach the molybdenum blue to a yellowish – green colour. The phospho-heteropoly blue was not extracted by any of the hydrocarbon (or chlorinated hydrocarbon) solvents tested.

The important criterion for the selection of a suitable solvent for studies of this kind, is that the solvent must possess selective extraction properties for phospho-heteropoly blue and silico-heteropoly blue *i.e.* the solvent must be capable of quantitatively extracting one without extracting the other. Of the solvents that were found to extract the phospho-heteropoly blue efficiently diethyl ether alone did not extract silico-heteropoly blue to any great extent, 1.7% of the silicate being extracted at the concentration tested. Ethyl acetate, although 100% efficient for the extraction of the phospho-heteropoly blue, was found to extract the silico-heteropoly blue to the extent of 16.7%. Silico-heteropoly blue, like phospho-heteropoly blue was not extracted by any of the hydrocarbons (or chlorinated hydrocarbons) tested.

TABLE II

EXTRACTION OF PHOSPHO- AND SILICO-HETEROPOLY BLUE BY DIETHYL ETHER

Phosphate present in aqueous phase before extraction μg	*Phosphate found in aqueous phase after extraction* μg	*Silicate present before extraction* μg	*Silicate found in solvent phase after extraction* μg
50	<5	20	<1
100	<5	30	<1
200	5	40	<1
300	7	50	<1
400	12	60	1

These preliminary studies indicated that among the solvents tested for selective solvent extraction of the heteropoly blue of phosphorus and silicon, diethyl ether was the most suitable. A detail study of the selective solvent extraction of phospho- and silico-heteropoly blue by this solvent was, therefore, made. The results of these studies (Table II) demonstrated that over a range of phosphate concentration (25 μg to 200 μg/ml), the phospho-heteropoly blue was efficiently extracted by diethyl ether. At the same time, the silico-heteropoly blue was not extracted to any significant extent between silicate concentrations of 10 μg to 25 μg/ml. The phosphate and silicate concentrations used in these studies included both the upper and lower limits of concentrations that the methods of estimation are capable of accurately determining.

TABLE III

ACCURACY OF CALIBRATION CURVES FOR PHOSPHORUS AND SILICON DETERMINATION

Phosphate content present μg	*Phosphate content found* μg	*Silicon content present* μg	*Silicon content found* μg
280	292	64	63
200	200	52	50
150	150	40	38
75	75	36	35
40	42	29	28

Fig. 1 shows the standard graph for the phospho-heteropoly blue in the solvent phase, while that for the silico-heteropoly blue after diethyl ether extraction, is given in Fig. 2. These graphs being linear, demonstrate that under the standard conditions adopted the blue colour in both the solvent phase and the aqueous phase was proportional to concentration. These calibration curves were tested at various concentrations of phosphate and silicate and were found to give accurate results (Table III).

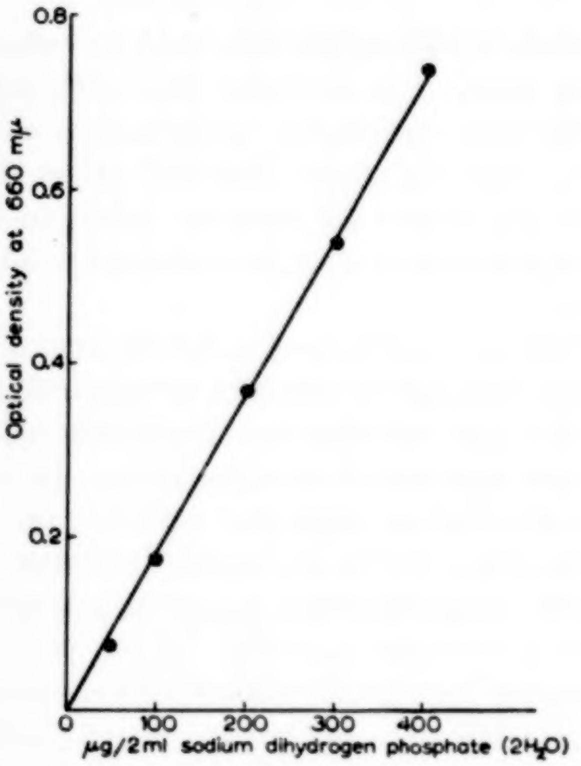

Fig. 1. Calibration graph for phosphorus determination after diethyl ether extraction of phospho-heteropoly blue.

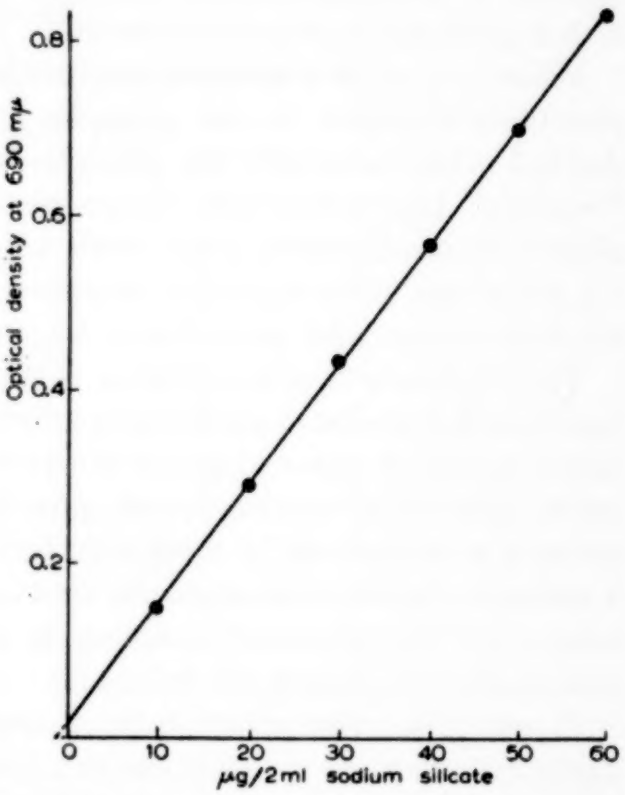

Fig. 2. Calibration graph for silicon determination after diethyl ether extraction of silico-heteropoly blue.

To conclude these studies, the recoveries of phosphate and silicate in mixtures of each other were determined by this method of determination utilizing the solvent extraction technique with diethyl ether. The results of these experiments, recorded in Table IV, demonstrate that this method of simultaneous determination of phosphorus and silicon is accurate and reproducible.

TABLE IV

SIMULTANEOUS DETERMINATION OF PHOSPHATE AND SILICATE IN MIXTURES OF EACH OTHER BY SOLVENT EXTRACTION OF PHOSPHO- AND SILICO-HETEROPOLY BLUE

Mixtures	*Phosphate present in mixture* μg	*Phosphate found after extraction* μg	*Silica present in mixture* μg	*Silica found after extraction* μg
A	400	390	55	56
B	300	315	37	38
C	200	196	27	25
D	100	97	40	39
E	50	51	10	10
F	25	26	13	13

DISCUSSION

The method described in this paper permits the simultaneous determination of phosphorus and silicon in the presence of each other. The major weakness of the method is that due to the relatively large volume of solvent that is employed in the extraction of the phospho-heteropoly blue, the method is not as sensitive in the determination of phosphorus as it is in the determination of silicon. Nevertheless, the method is capable of detecting accurately 12 μg/ml of phosphate. The method has the advantages of being simple, rapid and accurate.

When 1.0 ml of 1-amino-2-naphthol-4-sulphonic acid reagent was used to reduce phosphomolybdate to the phospho-heteropoly blue, it was found that although diethyl ether extracted the phospho-heteropoly blue completely, nevertheless as a "residual" blue colour was always present in the aqueous phase. This will affect the silicon determinations when both silicate and phosphate are present. Addition of 0.5 ml of the aminonaphthol sulphonic acid reagent however, gave excellent results for both silicon and phosphorus determinations.

The explanation of this finding is that under normal conditions, molybdic acid will react with 1-amino-2-naphthol-4-sulphonic acid reagent to produce a blue colour when excess of these reagents are present in the reaction mixture. Perchloric acid, when added in suitable amounts, prevents the development of this blue colour. In the present investigation, 2.0 ml perchloric acid (72%) when employed with 0.5 ml of 1-amino-2-naphthol-4-sulphonic acid reagent (0.2%) gave good results. However, if higher concentrations of reducing agent is used, proportionately larger amounts of perchloric acid should also be used.

It was found that when sodium sulphite solution (30%) was used as the reducing agent to effect the production of phospho- and silico-heteropoly blue instead of 1-amino-2-naphthol-4-sulphonic acid reagent, neither the phospho-heteropoly blue nor the silico-heteropoly blue could be extracted by ethyl acetate, *n*-propyl acetate, isopropyl acetate, *n*-butyl acetate, isobutyl acetate, isoamyl acetate, diethyl ether, petroleum ether (b.p. 40–60°), benzene, chloroform, carbon tetrachloride or tetrachloroethane.

ACKNOWLEDGEMENTS

The author wishes to thank Professor A. C. FRASER for facilities to carry out this investigation. The award of an I.C.I. Research Fellowship is gratefully acknowledged.

SUMMARY

An accurate and reproducible colorimetric method for the simultaneous determination of phosphorus and silicon in the presence of each other is reported. The method involves the selective extraction of phospho-heteropoly blue by diethyl ether.

RÉSUMÉ

Une méthode est décrite pour le dosage colorimétrique du phosphore et du silicium, en présence l'un de l'autre.

ZUSAMMENFASSUNG

Beschreibung einer colorimetrischen Methode zur Bestimmung von Phosphor und Silizium nebeneinander.

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THE SUPPRESSION OF CALCIUM INTERFERENCE IN THE FLAME PHOTOMETRIC DETERMINATION OF EXCHANGEABLE SODIUM IN SOILS

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INTRODUCTION

In the analysis of sodium using a flame photometer of the filter type, calcium usually interferes because of failure of the radiation filter used to isolate the sodium doublet at 589.0–589.6 mμ to completely exclude radiation from calcium. While this interference can be considerably reduced by the careful choice of filters[1], it cannot be completely eliminated. Steps must be taken to offset or prevent this interference either by applying a correction for the amount of calcium present, by removal of the calcium, or by chemical suppression of its radiation. This is particularly important for samples low in sodium and high in calcium, as is often the case in ammonium chloride leachates of soils. If a correction is made for calcium it is essential to ensure that no interference occurs with the calcium emission.

A method in which calcium interference is completely suppressed would have obvious advantages over one in which a correction is applied, particularly for samples where analysis for calcium is not required.

WILLIAMS[2] has shown that aluminium and phosphate both markedly depress calcium emission in ammonium chloride solution and WILLIAMS AND TWINE[3] have shown that these ions can suppress calcium interference with sodium in the analysis of plant material. The present investigation was made to examine the possibility of using aluminium or phosphate to suppress calcium interference in the flame photometric determination of sodium in ammonium chloride leachates of soils.

EXPERIMENTAL

The results were obtained using an E.E.L. flame photometer with a gelatine filter to isolate the sodium radiation at 589.0–589.6 mμ. The gases used were air and a proprietary bottled gas similar to "calor" gas.

Stock solutions were prepared as follows:

Calcium: Calcium carbonate was dissolved in a slight excess of hydrochloric acid. The solution was boiled to expel carbon dioxide and, after cooling, made to volume.

Aluminium chloride: Aluminium metal was dissolved in a slight excess of hydrochloric acid and the solution adjusted to volume.

Other stock solutions were prepared from ammonium chloride, sodium chloride, ammonium dihydrogen phosphate and aluminium ammonium sulphate.

Soils were leached with normal ammonium chloride and sodium and calcium determined as described by WILLIAMS[2] except that to allow comparisons to be made, lanthanum chloride was not added before adjusting to volume, but was added in 1 ml of solution to a 20-ml aliquot.

RESULTS AND DISCUSSION

Suppression of calcium interference

Results of the examination of solutions to test the effect of aluminium and phosphate on the suppression of calcium interference with sodium in normal ammonium chloride solution are given in Table I.

TABLE I

THE EFFECT OF ALUMINIUM AND PHOSPHATE ON THE INTERFERENCE OF CALCIUM WITH 2.5 p.p.m. OF SODIUM IN NORMAL AMMONIUM CHLORIDE SOLUTION

Addition p.p.m.	*Galvanometer reading*			
	Calcium added p.p.m.			
	0	*50*	*100*	*200*
Nil	29	35	41	53
250 Al	29	31	32	45
400 Al	30	30	30	34
400 Al + 400 P	31	31	31	32
500 Al[a]	31	32	32	33
800 Al + 800 P[b]	38	38	38	38

[a] Added as aluminium ammonium sulphate.

[b] Added as aluminium ammonium sulphate and phosphoric acid.

These results show that aluminium alone and aluminium together with phosphate were effective in suppressing interference from calcium, but for complete suppression of interference in solutions containing up to 200 p.p.m. of calcium, aluminium and phosphorus in excess of 400 p.p.m. of each were necessary. Complete suppression at this level of calcium was obtained with approximately 800 p.p.m. of both aluminium and phosphorus added as a solution of ammonium alum and phosphoric acid. Further tests showed that these concentrations gave complete suppression of interference from 250 p.p.m. of calcium while with 500 p.p.m. of calcium the galvanometer reading was increased only from 38 to 40.

These results suggest that satisfactory suppression of calcium interference in ammonium chloride leachates of soils should be achieved by the addition of similar amounts of aluminium and phosphate. This can be done by the addition of 2 ml of a solution containing 15 g of aluminium ammonium sulphate (ammonium alum) and 2 ml of phosphoric acid ($d = 1.70$) per 100 ml to 20 ml of ammonium chloride leachate. The sodium concentration can then be determined by reference to a calibration curve prepared from normal ammonium chloride standards to which corresponding amounts of the aluminium–phosphoric acid solution have been added.

Examination of soils

As a check on the proposed method a group of soils was leached with normal ammonium chloride, and sodium was determined with the flame photometer both by suppression of calcium interference as proposed, and by applying a correction for calcium interference after reading both sodium and calcium following addition of 2000 p.p.m. of lanthanum as suggested by WILLIAMS[2]. The results are given in Table II.

TABLE II

A COMPARISON BETWEEN EXCHANGEABLE SODIUM IN SOILS DETERMINED BY SUPPRESSION OF CALCIUM INTERFERENCE AND BY CORRECTION FOR CALCIUM INTERFERENCE

Sample No.	*Exchangeable calcium m.e. per 100 g*	*Exchangeable sodium m.e. per 100 g*	
		Ca correction	*Ca suppression*
1	56.6	0.521	0.551
2	40.8	5.65	5.76
3	36.8	0.311	0.316
4	35.2	0.109	0.125
5	31.9	2.97	3.01
6	24.0	0.085	0.087
7	21.4	0.371	0.380
8	16.1	0.330	0.381
9	13.5	0.082	0.078
10	11.5	2.14	2.11
11	10.2	0.127	0.122
12	10.0	0.513	0.522
13	9.4	0.267	0.249
14	7.8	0.197	0.207
15	6.6	0.133	0.139
16	4.0	0.172	0.178
17	3.3	0.118	0.122
18	0.5	0.061	0.061

These results show that satisfactory agreement was obtained between the two methods. In general the values obtained when calcium interference was suppressed tended to be slightly higher than when a correction was made. However, the difference was small and the results indicate that the aluminium–phosphoric acid solution had given satisfactory suppression of calcium interference over the whole range of soils which included some with high calcium: sodium ratios.

SUMMARY

An examination of the effects of aluminium and phosphate on the interference of calcium with sodium analysis using a flame photometer of the filter type showed that these ions could be used to suppress this interference.

A method is proposed for the satisfactory suppression of calcium interference in the determination of exchangeable sodium in ammonium chloride leachates of soils.

RÉSUMÉ

L'emploi de l'aluminium et du phosphate permet de supprimer l'interférence du calcium lors du dosage du sodium par photométrie de flamme. Une méthode est proposée pour le dosage du sodium dans des terres.

ZUSAMMENFASSUNG

Die durch Calcium verursachte Störung der flammenphotometrischen Bestimmung von Natrium kann durch Zusatz von Aluminium und Phosphat ausgeschaltet werden. Es wird eine Methode beschrieben zur Bestimmung von Natrium in Erdproben.

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DETERMINATION OF METAL IONS BY MEANS OF TAA AND EDTA

II. DETERMINATION OF COPPER

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INTRODUCTION

In a previous paper[1] attention was drawn to new possibilities for rapid metal determinations by means of the combined use of thioacetamide (TAA) and ethylenediaminetetraacetic acid (EDTA). For the determination of copper in the TAA–EDTA system, the use of EDTA and calcium chloride is not necessary, because copper, being a group II element, precipitates with TAA in acid medium.

The spectrophotometric method with aminoacetic acid, described by ZIEGLER[2] is preferred for the determination of copper. According to ZIEGLER, only a few elements of the third group interfere in this method. The molar extinction coefficient (34.3 for the flat-maximum at 735 mμ, as measured with a Unicam SP 500 spectrophotometer) is somewhat low, but a more sensitive method which is not subject to interferences is not available. The method, however, is entirely acceptable for the present purpose where intermediate amounts of copper rather than traces were involved. ZIEGLER's statement that the colour is very stable and that small amounts of nitric acid do not interfere was confirmed. This is very important because the metal sulfides have to be dissolved by means of nitric acid.

The observations of ZIEGLER permitted the assumption that addition of TAA to an acid solution containing a mixture of metal ions, would separate copper from all the elements that interfere with its determination by means of aminoacetic acid. Dissolution of the precipitate in nitric acid and treatment according to the method of ZIEGLER would then give the correct copper content of the mixture.

EXPERIMENTAL

Reagents

Aminoacetic acid, AnalaR, a 10% solution in water containing 4% sodium citrate.

Procedure

The determinations are carried out in 15-ml centrifuge tubes. To 4–8 ml of a neutral (or slightly acid) solution, containing not less than 2.5 mg copper, add 1–2 ml of 4 *N* hydrochloric acid and 1 ml of aqueous 6% TAA solution. Heat for 20 min in a water bath at 90°. Centrifuge and remove the supernatant liquid by suction through a G4 glass filter stick as shown in Fig. 1 of the previous paper[1]. Remove as little as possible of the precipitate from the centrifuge tube into the glass filter. Wash the precipitate after filtration three times with 1–2 ml of water and remove the washing water in the same way. Dissolve the precipitate in the centrifuge tube and on the filter in a few drops of 60% nitric acid. Place the combined solutions in a 50-ml volumetric flask. Add 25 ml of the colour reagent and dilute to the mark. The sodium citrate in the reagent solution adjusts the pH of the final solution to between 2.9 and 4.1. Measure the extinction in a 4-cm cell in a Unicam SP 500 spectrophotometer at 735 mμ. In some cases (especially when lead was present), it was necessary to centrifuge the coloured solution before measuring the extinction.

Remarks

I. The decanted liquids always contain small (not always visible) amounts of copper sulphide. Therefore filtration is essential. When polypropylene centrifuge tubes were used, it seemed possible in some cases to discard the decanted liquid directly without using glass filters. II. It is advisable to use a good electric centrifuge (*e.g.* 3000 r.p.m.).

RESULTS

I. *Determination in presence of group II elements*

The results of the determinations of copper in presence of other group II elements are shown in Table I.

TABLE I

DETERMINATION OF COPPER IN PRESENCE OF OTHER GROUP II ELEMENTS

Amounts of other elements in mg							*mg Cu present*	*mg Cu found*	*error in %*
Hg	*Pb*	*Cd*	*As*	*Sb*	*Sn*	*Bi*			
			4	4	4		4.00	4.00	0.0
			4	4	4		4.00	4.02	+0.5
			4	4	4		4.00	3.98	−0.5
4	4	4					4.00	3.98	−0.5
4	4	6					4.00	3.98	−0.5
16	16	16					2.50	2.52	+0.8
16	16	16					2.50	2.52	+0.8
4	4	4	4	4	4		2.50[a]	2.45	−2.0
4	4	4	4	4	4		2.50[a]	2.45	−2.0
			16	16	16		2.50[a]	2.45	−2.0
			16	16	16		2.50[a]	2.50	0.0
4	4	4	4	4	4		2.50	2.52	+0.8
4	4	4	4	4	4		2.50	2.50	0.0
			16	16	16		2.50	2.52	+0.8
						16	5.00	5.16	+3.2
						16	5.00	5.02	+0.4
						16	5.00	5.26	+5.2

[a] Experiments carried out in polypropylene centrifuge tubes (the decant liquid was discarded without filtration).

Table I shows that copper can be determined with fair accuracy in presence of twenty-fold amounts of other group II elements other than bismuth, which interferes causing positive errors.

The lowest amount of copper that can be determined accurately by this method is 2.5 mg, because of the low sensitivity of the spectrophotometric method. Smaller copper concentrations can be determined similarly by taking larger volumes. In Table II the results of the determinations of 2.5 mg copper are shown; 100-ml centrifuge tubes were used and 10–20 ml of hydrochloric acid was added but the method was otherwise the same as described above. In this way copper concentrations as small as $4 \cdot 10^{-4}$ M were determined with fair accuracy.

TABLE II

DETERMINATIONS OF SMALLER COPPER CONCENTRATIONS

Amounts of other elements in mg						*mg Cu present*	*mg Cu found*	*error in %*
Hg	*Pb*	*Cd*	*As*	*Sb*	*Sn*			
2	2	2				2.50	2.49	—0.4
			2	2	2	2.50	2.50	0.0
			2	2	2	2.50	2.49	—0.4

II. *Determination of copper in presence of group III elements*

KRIJN[3] has already described the macro determination of copper by precipitation with TAA in the presence of group III elements and subsequent iodometric determination. Group II elements generally interfere with this iodometric determination. As was expected, determinations of copper by the method proposed in the present paper showed that group III elements do not interfere.

SUMMARY

Copper can be determined in presence of the common group II and group III elements by precipitation with TAA in acid solution and subsequent spectrophotometric determination as the copper(II)-aminoacetic acid complex. Only bismuth interferes. Copper was determined in concentrations as small as $4 \cdot 10^{-4}$ M and in presence of As, Sb, Sn, Pb, Cd, Hg and all group III elements.

RÉSUMÉ

Le cuivre peut être dosé en présence des éléments les plus communs des groupes II et III, par précipitation avec TAA, en solution acide, suivie d'une détermination spectrophotométrique du complexe cuivre(II)-acide aminoacétique. Seul le bismuth gène.

ZUSAMMENFASSUNG

Kupfer kann in Gegenwart der häufig vorkommenden Elemente der zweiten und dritten Gruppe quantitativ bestimmt werden durch Fällung mit TAA in säurer Lösung und folgende spektrophotometrische Bestimmung als Kupfer(II)-aminoessigsäures Komplex. Nur Wismut stört die spektrophotometrische Bestimmung. Dieses Metall darf also nicht anwesend sein. Kupfer wurde nach dieser Methode in Konzentrationen bis $4 \cdot 10^{-4}$ M bestimmt, in Anwesenheit von As, Sb, Sn, Pb, Cd, Hg und die Metalle der dritten Gruppe.

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THE RELATION OF CATALYST ACIDITY TO THE ELECTRODE POTENTIAL RECORDED IN AN AUTOMATIC TITRATION*

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The strength and amount of surface acidity on catalysts has been a subject of considerable interest to the petroleum processing industry[1-9]. It has been proposed[2] that the acid sites are effective in the formation of carbonium ions from hydrocarbons, and relations have been found[3,5,9] between surface acidity and cracking or polymerization activity. Of the various methods reported for the determination of catalyst acidity and strength, the titration of a non-aqueous suspension with *n*-butylamine, with the use of indicators of various pK_a values for the end-point determination, has received considerable attention in this laboratory. The original method described by BENESI[1] involved the batchwise titration of a suspension, followed by the addition of indicators to portions of the suspension. However, two disadvantages of the use of indicators in the determination were apparent. These were (a) the limitation of the method to materials with sufficient lack of color to enable indicator color changes to be seen, and (b) the tediousness of the technique, which involves careful manipulations and observations by trained personnel. The first of these objections can be mitigated by mixing light colored standards with the samples. This modification of the technique, however, intensifies the second factor. These limitations suggested an investigation of a potentiometric titration technique which would be equally applicable to dark and light colored catalysts, involve essentially no manual manipulations, and give a permanent record of the test on a recorder chart strip.

Titration of an aqueous suspension of silica has been described by BOLT[10], in which a glass electrode was immersed in the suspension and a calomel electrode was connected by a bridge of 3% agar in the silica dialyzate. Potentiometric titrations in aqueous media have also been described with regard to the total exchange capacity of soils[11] and ion-exchange resins[12]. Batchwise titration of clay, alumina, and quartz in ethanol have been described by GOATES, ANDERSON AND WILLIS[13,14]. The potentiometric titration of clay and resin suspensions in alcohol–water–aniline mixtures was described by GANGULY, MUKHERJEE AND GHOSH[15]. The direct application of these methods offered little or no improvement in either speed or automatic operation over the procedure of batchwise butylamine equilibration and indicator tests. Since catalyst samples characterized in this laboratory by the indicator technique were available (data in Figs. 5 and 6), it was decided to approach the problem by a continuous and recorded titration. After experimentation with various solvents, electrodes, and methods of instrumentation, a technique was found for titrating ground catalyst suspensions with a dilute solution of butylamine in acetonitrile, in such a manner as to yield curves characteristic of the catalysts. The titration can be performed, and the data recorded, with an automatic titrator, so that operator time is involved only in the preparation of samples, the setting up of the instrument, and the interpretation of the recorded potential curve.

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EXPERIMENTAL

In order to find the best conditions for a completely automatic method of measurement, various conditions were investigated regarding the feed rate of the reagent solution to the catalyst, the preparation of a homogeneous catalyst slurry, the rate of stirring, and the optimum normality of the titrating base. Within limits, any of the experimental conditions may be varied, and still yield titration curves clearly differentiating catalysts of various acidity characteristics. In the course of the work described here changes were made to the equilibration period at the start of the experiment, and these affected the initial potential readings shown in various figures. The following procedure is suggested as a most suitable way of handling this test on a routine basis.

One gram of sample, ground to pass a 200-mesh sieve, is pretreated by calcination in a 25-ml Erlenmeyer flask for three hours at 500°. The flask, while still in the furnace, is stoppered with a standard taper stopper, then immediately placed in a desiccator to cool. It is transferred quantitatively with reagent grade acetonitrile into a 250-ml beaker and diluted to a total volume of 150 ml. Standard glass and calomel electrodes are immersed in the slurry and a glass stirrer set to a speed just below that creating turbulence. After a 5-min equilibration period, the titration is started, with 0.008 molar butylamine in acetonitrile introduced to the slurry at a constant rate of 0.4 ml per minute. A Precision-Dow Dual Recordomatic Titrometer provides the mechanism for the constant rate of flow of titrant and the recording of the potential curve. The catalyst samples used in these experiments are listed in Table I.

TABLE I

CATALYST SAMPLES

Name	*Source*	*Principal components*	*Area*
S-46	Houdry Co., Philadelphia	87–13% Silica–alumina	315 m²/g
AAA	American Cyanamid Co., New York	75–25% Silica–alumina	452 m²/g
DA-5 Silica–magnesia	Davison Chemical Co., Baltimore	70–30% Silica–magnesia	500 m²/g
F-10	Aluminum Co. of America, Pittsburgh	Alumina	125 m²/g
Cabosil M-5	Godfrey L. Cabot, Inc., Boston	Silica	175–200 m²/g

RESULTS

Comparative data for typical catalyst substrates

The recorded data for four catalyst samples, including three different types, are shown in Fig. 1. The four samples were all titrated under the same experimental conditions. Both Houdry S-46 and Aerocat Triple A silica–alumina show similar but distinguishable curves. It was known from results using a butylamine batchwise titration and indicators on a spot plate that the S-46 contained about 0.19 mequivs. of acid sites strong enough to turn an indicator of pK_a —8.2, and a distribution of sites to a total of 0.33 mequivs./g. The Triple A contained about 0.30 mequivs. of the very strong sites, and a total of about 0.35 mequivs./g. The titration curves qualitatively and semi-quantitatively agreed with these results.

The silica–magnesia sample had a surface with only weakly acidic sites, as determined with Hammett indicators. This was again found to be the case when it was titrated electrometrically, as the initial electrode potential was approximately half that found for a system containing strong surface acidity. The silica–magnesia electrometric titration curve decreased in slope very slowly, indicating a large amount of weak acid sites. This corresponded to the titration with indicators in which 1.2 mequivs./g of weakly acidic sites were noted.

The F-10 alumina sample had about 0.04 mequivs./g of weak acid sites. The titration curve, which is easily distinguished from the silica–magnesia, indicated a total acidity somewhat in excess of this value.

When replicate samples were titrated under the same conditions, the reproducibility of the electrode potential curve was ±5 mV.

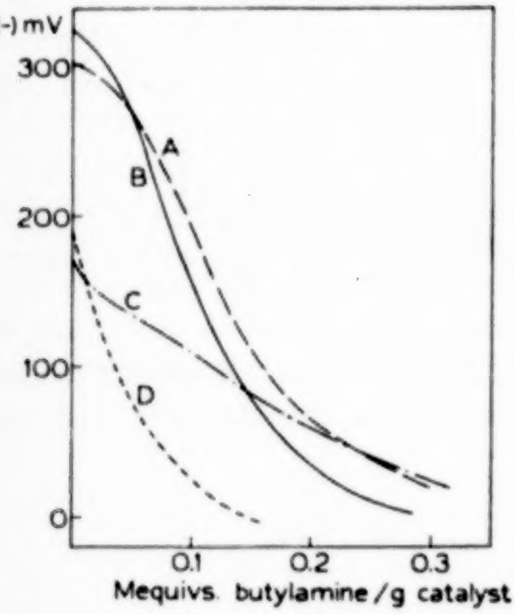

Fig. 1. Titration of typical catalyst bases. A. Triple A silica–alumina; B. S-46 silica–alumina; C. silica–magnesia; D. F-10 alumina.

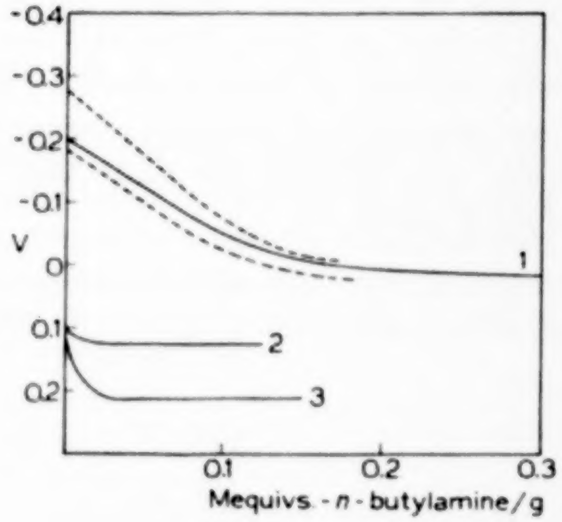

Fig. 2. The application of the titration to dark colored, metal promoted, catalyst samples.

Pre-equilibrated samples

As the titrations were done with a slow but constant feed of *n*-butylamine titrant, the relation of these results to batch titration results depended on the effective equilibration of the slurry with the added titrant. Samples of Houdry S-46 silica–alumina catalyst were contacted with various amounts of butylamine by shaking for three hours at room temperature, before the titration. The results in Table II compare the influence of pre-equilibrated and titrated base on the electrode potential. The first incremental addition, 0.025 mequivs./g appeared to need a slower feed rate for equilibration. However, the equilibration was satisfactory for greater amounts of amine.

TABLE II

A COMPARISON OF THE EFFECTS OF PRE-EQUILIBRATION, AND TITRATION WITH BASE, ON THE ELECTRODE POTENTIAL OF A HOUDRY S-46 SILICA–ALUMINA CATALYST SLURRY

Amounts of added butylamine	*Change in electrode potential*	
	Pre-equilibration	*Continuous automatic titration*
0.025 mequivs./g	90 mV	50 mV
0.050 mequivs./g	130 mV	130 mV
0.100 mequivs./g	230 mV	250 mV
0.150 mequivs./g	290 mV	320 mV

Applications to metal promoted samples

Since the major types of acid surface catalysts can readily be differentiated by the automatic titration technique, an unknown sample can be characterized by the similarity of its titration curve to that of other materials of known acidity. In Fig. 2, the experimental titration curves are shown for three dark colored, metal promoted, catalyst samples whose acidity could not be directly determined with indicators. As these catalysts are presently part of an experimental program of commercial interest they cannot be more explicitly defined here. The illustration merely shows the application of the technique to this type of sample. Sample 1 falls between the curves of the unpromoted catalyst pre-equilibrated with 0.075 and 0.100 mequivs. of butylamine per gram. Therefore, 0.075 to 0.100 mequivs./g of strong acid sites have been covered or deactivated by the promotion treatment, leaving approximately 0.20 mequivs./g of strong and medium strength acid sites. In contrast, the sample 2 curve of a different substrate shows no appreciable acidity, and sample 3 appears slightly basic.

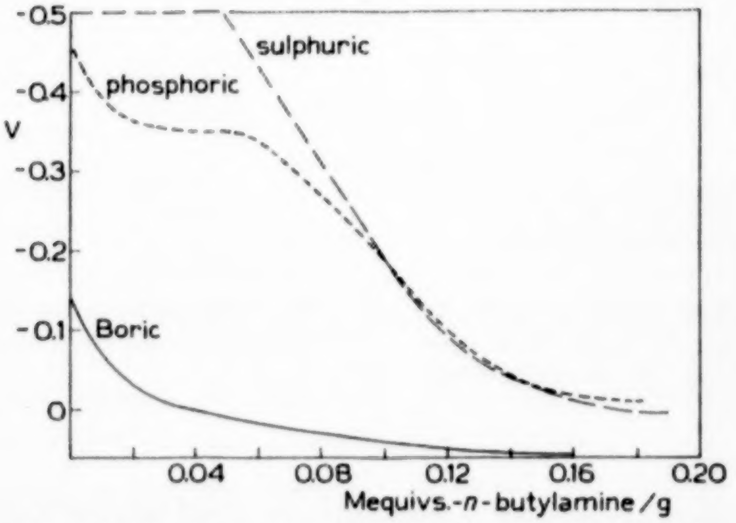

Fig. 3. The titration of mounted mineral acids on silica.

Titration of mounted acid samples

In Fig. 3, the curves depict the titration of three mineral acids mounted on Cabosil M-5, a non-porous silica. The technique described by BENESI[16] was used to contact the silica with 0.1 millimoles of phosphoric, and 0.2 millimoles of boric acid per gram of catalyst. The curves indicate the strength of the acids in the correct order, the initial voltage of the mounted sulfuric being off-scale of the instrument. If the available mounted acid was the same as the amount impregnated, the first ionizable hydrogen of the sulfuric and phosphoric acids was titrated in the range shown, but only a portion of one hydrogen of the boric acid was titrated. A similar observation was made by BENESI[1] for the amine titration with Hammett indicators.

THEORY AND TREATMENT OF DATA

The physical system in this measurement consists of a dispersed solid in a non-aqueous solvent. The measured electrode potential may arise from several sources including;

(a) The standard electrode potential of the calomel electrode, (*i.e.* the $Hg-HgCl_2$ interface).

(b) The liquid junction potential between the aqueous potassium chloride solution inside the sleeve of the calomel electrode and the dispersion in acetonitrile outside the electrode.

(c) The difference in potential across the glass membrane separating the dispersion in acetonitrile and the aqueous buffer solution inside the electrode, and

(d) The potential of the sensing electrode within the glass electrode (*i.e.* the $Ag-AgCl$ interface).

Since (a) remains unchanged during an experiment, and (d) responds directly to (c) the effects (b) and (c) may account for the potentiometric curve. The effect (b), if present, does not appear to change appreciably during a titration. Thus the addition of butylamine solution to a non-acidic solid dispersion, or to the solvent alone, did not change the electrode potential to any extent.

Therefore, it appears that the electrode potential is determined primarily by the acid environment given to the outside of the glass electrode membrane by immersion in the finely divided acid-surfaced particles. The measured electrode potential may reflect the properties of the solid dispersion with regard to its weight concentration, particle size, strength and number of surface acid sites, and other surface effects.

TABLE III

EFFECT OF PARTICLE SIZE ON THE ELECTRODE POTENTIAL

Particle diameters-microns	*Measured initial potential V*	*Mequivs. of n-butylamine per gram of solid required to produce zero potential*
590–840	—0.08	0.01
297–420	—0.15	0.015
149–297	—0.18	0.06
105–149	—0.25	0.07
74–105	—0.31	0.14
44–74	—0.37	0.25
Smaller than 44	—0.37	0.25

In practice, the effect of certain of these factors may be determined, and thereafter held constant. For example, tests were made (Table III) of the effect of changing particle size on the electrode potential of a Houdry S-46 sample and it was found that a minimum particle size must be used before the maximum effect of the slurry on the electrode potential appears. Of the other factors, the strength of the surface acid is the variable with the greatest effect on the electrode potential.

In the interpretation of these data it was desired to plot the curves in a manner more directly showing the distribution of acid strength on the catalyst surface than the recorded potential curve. The topographical similarity of these recorded curves to the differential heats of adsorption of butylamine on attapulgite obtained by CHESSICK AND ZETTLEMOYER[17] was noted. Following a procedure used by DRAIN AND MORRISON[18] for heats of adsorption of argon on rutile, CHESSICK AND ZETTLEMOYER calculated a site energy distribution function $g(E)$ from the slope of the plot of the differential heat of adsorption (ΔH_d) against the moles of adsorbed butylamine, as

$$\frac{\mathrm{d}N}{\mathrm{d}(\Delta H_d)} = g(\Delta H_d)$$

Without implying an identity of thermodynamic quantities, the potentiometric titration curves may be treated in an analogous fashion by a plot of $\mathrm{d}N/\mathrm{d}E$ *vs.* $\mathrm{d}E$, where N is the moles of added butylamine, and E is the electrode potential. Differential plots of this type are compared in the Figs. 4 and 5 with histograms of the acidity distribution of the same materials as obtained by a modification of the Benesi technique, in which the indicator is added to a dried portion of the catalyst on a spot plate. The differential representation seems to yield in these cases a satisfactory picture of the acid strength distribution on the catalyst surface. From the theoretical point of view, a more complex treatment of the data is necessary, but in this simple

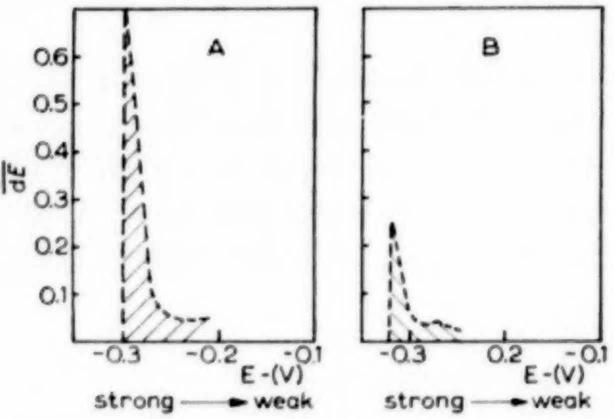

Fig. 4. A comparison of the differential plots of the titrations with the acidity distribution found with Hammett indicators. A. Triple A silica-alumina; B. S-46 silica-alumina.

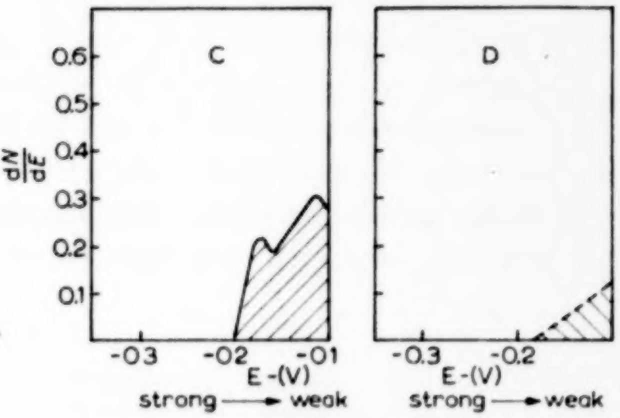

Fig. 5. A comparison of the differential plots of the titrations with the distribution found with Hammett indicators. C. silica-magnesia; D. F-10 alumina.

treatment advantage is taken of the primary sensitivity of the electrode potential to the strength of the surface acid sites in the catalyst slurry.

CONCLUSIONS

The continuous and recorded electrometric titration of slurries described here provides a convenient and reproducible method of screening prepared and treated solid catalyst for surface acid strength and concentration. The measurement is most readily used in the comparative testing of unknown samples against standards whose acidity has been characterized by an alternate method. It is particularly valuable to laboratory operations in which surface acidity data are of continuous interest for a flow of samples, as the technique is largely automated.

ACKNOWLEDGEMENT

The authors wish to thank Dr. N. D. COGGESHALL, Gulf Research and Development Company, for his guidance and suggestions.

SUMMARY

The potentiometric titration of catalyst slurries in acetonitrile has been used for the determination of the surface acidity of catalysts. The technique is equally applicable to dark and light colored catalysts, involves essentially no manual manipulations, and gives a permanent record of the test on a recorder chart strip. The potentiometric titration curves of various types of catalysts and catalyst substrates with butylamine are shown. The titration curves are consistent with knowledge of catalyst acidity from batchwise titration with indicators; and are sensitive to previous equilibration with the basic titrant and to the covering of surface acid by metallic promoters. The automatic titration is a useful screening tool for characterization of samples in catalyst development programs.

RÉSUMÉ

La détermination de l'acidité de la surface des catalyseurs peut être effectuée par titrage potentiométrique au moyen de la butylamine. Une méthode automatique est décrite.

ZUSAMMENFASSUNG

Die Bestimmung des Säuregrades der Oberfläche von Katalysatoren kann durch potentiometrische Titration mit Butylamin erfolgen. Es wird eine automatische Methode beschrieben.

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STUDIES IN POLAROGRAPHIC ANALYSIS

II. AMPEROMETRIC TITRATION OF TELLURITE WITH POTASSIUM PERMANGANATE

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The potentiometric titration of tellurite with potassium permanganate has been studied under a variety of conditions[1,2]. Good results can be obtained when the titrations are performed in 0.1 *N* sodium hydroxide, and when the titrated solutions are 0.1 to 10^{-4} *N*. These concentrations lie within the range of polarographic analysis, hence we have examined the amperometric titration of tellurite with permanganate in alkaline solutions. The titration is possible because the diffusion currents of permanganate[3] and tellurite[4] vary with the concentration of the reducible materials. Amperometric titrations are of practical importance because of their simplicity and rapidity; the equivalence point can be determined from a few readings on each side of the end-point. Moreover, it is not necessary to titrate slowly near the end-point, whereas in potentiometric titrations the equilibrium becomes sluggish as the concentrations of the reactants decrease.

EXPERIMENTAL

Solutions

Potassium permanganate solutions 0.1396 and 0.090 *N* were prepared by the method of STAMM[5] and standardised with sodium oxalate; 0.0108 and 0.005 *N* solutions were prepared by appropriate dilution.

Sodium tellurite solutions 0.0605 and 0.0518 *N* were prepared by dissolving the solid in twice-distilled water and standardising against potassium permanganate[2]; $6.05 \cdot 10^{-4}$ up to $2.07 \cdot 10^{-3}$ *N* solutions were prepared by dilution with twice-distilled water.

Apparatus and technique

The diffusion current was measured by a Radiometer Polarograph. The capillary characteristics measured in open circuit at a mercury height of 40 cm were $m = 1.992$ mg/sec and $t = 3.33$ sec. For a titration, 5 ml of the *ca.* 10^{-3} *M* tellurite solution was made 0.05 or 0.1 *N* to sodium hydroxide and placed in the polarographic cell and purified nitrogen was bubbled through it for about 20 min. The nitrogen stream was then placed over the solution. The applied potential was adjusted to —0.8 V, —1 V, —1.4 V or —1.7 V *vs.* S.C.E. After the diffusion current of the tellurite solution alone had been measured, the permanganate solution was added from a burette. Nitrogen gas was then bubbled for two min in order to mix the reactants and to remove any dissolved oxygen. After each addition of the permanganate, the diffusion current was recorded. The diffusion current corrected for dilution was calculated and plotted against the volume of permanganate added. The end-point corresponding to the intersection of the two branches of the titration curve was obtained by interpolation.

RESULTS AND DISCUSSION

The amperometric titration curves of tellurite in alkaline solutions by potassium permanganate are shown in Figs. 1 and 2. The curves in Fig. 1 show the titration of tellurite solutions with 0.00216 M potassium permanganate solution in presence of 0.05 N - 0.1 N NaOH at —0.8 and —1.0 V; the curve is approximately reversed L-shaped. At these potentials neither tellurite nor tellurate (obtained by the oxidation or initially added to combine with the manganese(IV) formed) are reduced at the dropping mercury electrode. The initial current (—0.5 to 0.7 μA) represents the residual current. The current then increases slowly along branch A of the curves as the permanganate solution is added because manganese(IV) produced from the reaction,

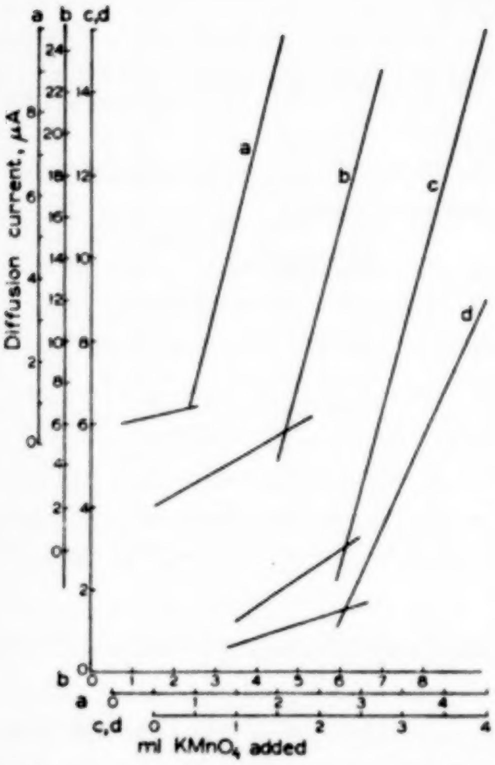

Fig. 1. a. 10 ml $6.05 \cdot 10^{-4}$ N Te^{+4} titrated with 0.00648 N $KMnO_4$ in 0.1 N NaOH, in absence of telluric acid at —0.8 V. b. 5 ml $6.05 \cdot 10^{-3}$ N Te^{+4} titrated similarly in presence of telluric acid at —1 V. c. 10 ml $1.513 \cdot 10^{-3}$ N Te^{+4} titrated similarly in presence of telluric acid at —0.8 V. d. As in c in absence of telluric acid.

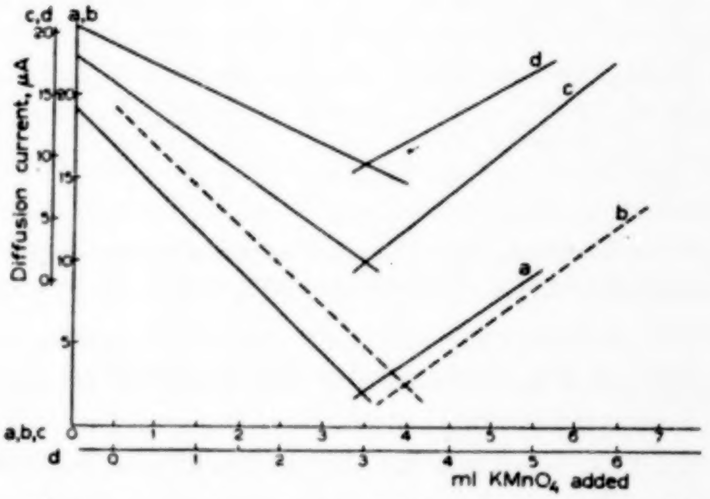

Fig. 2. 5 ml $2.07 \cdot 10^{-3}$ N Te^{+4} titrated with $3 \cdot 10^{-3}$ N $KMnO_4$ in 0.05 N NaOH at a, —1.7 V; b, c, d, —1.4 V.

$$3\ Te^{+4} + 2\ Mn^{+7} \rightarrow 3\ Te^{+6} + 2\ Mn^{+4}$$

is reduced at the dropping mercury electrode (D.M.E.) to manganese(II) when telluric acid is present.

When all the tellurite has been oxidised, the current increases rapidly, owing to the reduction of the permanganate added, along branch B of the titration curve. The intersect of the two branches gives the end-point.

The curves obtained at —1.4 V are V-shaped (*cf.* Fig. 2); at this potential tellurite is reduced at the D.M.E. and the initial current corresponds to the tellurium(IV) concentration. As permanganate is added tellurite is oxidised but tellurate is not reduced at —1.4 V at the D.M.E., and the current decreases continuously as the tellurium(IV) concentration decreases. When the end-point has been passed, the current increases again owing to the reduction of the excess permanganate. As in the

TABLE I

Vol. and normality of tellurite	*Alkalinity N*	*Normality*[a] *of $KMnO_4$ (N)*	*Vol. of $KMnO_4$ to tellurite*		*Error %*	*Remarks*
			Potentiometric	*Amperometric*		
10 ml $1.513 \cdot 10^{-3}$ *N*	0.1	0.00648 *N*	2.335	2.325	—0.43	—0.80 V telluric acid
10 ml $6.05 \cdot 10^{-4}$ *N*	0.1	0.00648 *N*	0.934	0.938	+0.43	—0.8 V no telluric acid
10 ml $1.513 \cdot 10^{-3}$ *N*	0.1	0.00648 *N*	2.335	2.325	—0.43	—0.8 V no telluric acid
5 ml $6.05 \cdot 10^{-3}$ *N*	0.1	0.00648 *N*	4.669	4.70	+0.66	—1 V telluric acid
5 ml $2.07 \cdot 10^{-3}$ *N*	0.05	$3 \cdot 10^{-3}$ *N*	3.45	3.470	+0.58	—1.7 V
5 ml $2.07 \cdot 10^{-3}$ *N*	0.05	$3 \cdot 10^{-3}$ *N*	3.45	3.475	+0.72	—1.4 V
5 ml $2.07 \cdot 10^{-3}$ *N*	0.05	$3 \cdot 10^{-3}$ *N*	3.45	3.44	—0.29	—1.4 V
5 ml $2.07 \cdot 10^{-3}$ *N*	0.05	$3 \cdot 10^{-3}$ *N*	3.45	3.437	—0.38	—1.4 V

[a] Normality is based on a valency change = 3 *i.e.* from 7 to 4. The values were obtained by multiplying the normalities determined by the oxalate method (*i.e.* 0.0108 and 0.005) by 0.6.

case of Fig. 1 the end-point is obtained by extrapolating the linear portions of the V-shaped curve.

In these titrations the normality of NaOH was kept at 0.05 – 0.1 *N*; at this alkalinity dilute tellurite solutions reduce permanganate to manganese dioxide. At higher alkalinities, manganate is also formed as a reduction product and erroneous results are obtained.

The end-points obtained from the titration curves are shown in the third column of Table I. The amperometric method gives results which are in reasonable agreement with those of the potentiometric method. The amperometric method has the advantage of speed; a titration requires only 15 min after deaerating the solution whereas the potentiometric titration needs 30–40 min.

SUMMARY

Tellurite was titrated amperometrically with permanganate in presence of 0.05 – 0.1 *N* NaOH and in presence or absence of telluric acid. At —0.8 and —1 V reversed L-shaped curves were obtained; at —1.4 V, the curves were V-shaped. The results agreed with those of potentiometric titrations.

RÉSUMÉ

Le titrage de tellurite a été effectué par ampérométrie, au moyen de permanganate, en milieu alcalin. Les résultats trouvés sont satisfaisants et concordent avec ceux obtenus par potentiométrie.

ZUSAMMENFASSUNG

Beschreibung eines amperometrischen Titrationsverfahrens zur Bestimmung von Tellurit mit Permanganat in alkalischer Lösung. Es werden die gleichen Resultate erhalten wie mit der potentiometrischen Methode.

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Short Communications

The recovery of chloroform from dithizone residues

The use of large quantities of chloroform solutions of dithizone for determining lead and zinc in agricultural and geochemical materials necessitated some means for the recovery of chloroform.

Extraction with concentrated sulphuric acid, followed by distillation from lime has been employed by BIDDLE[1] and HUBBARD[2] for the recovery of chloroform from dithizone residues. MULLIN AND RILEY[3] found that prolonged contact of chloroform with either sulphuric acid or lime rendered it unfit for the preparation of dithizone solutions. Chloroform that was badly contaminated with photochemical oxidation products when purified by the above procedure caused immediate oxidation of dithizone. MULLIN AND RILEY[3] obtained pure, stable chloroform by distilling the dithizone residues through a layer of 10% sodium sulphite solution; shaking the distillate with 3% hydroxylamine hydrochloride solution or 10% sodium sulphite solution and distilling the product from lime or active charcoal into 1% of its volume of ethyl alcohol.

The recovery method proposed here involves breaking down the lead and zinc dithizonates with alkaline EDTA solution. The lead and zinc EDTA complexes and the dithizone go into the aqueous phase leaving oxidised dithizone (diphenylthiocarbodiazone) in the chloroform. Phosgene is hydrolysed by the alkaline solution to ammonium chloride and ammonium carbonate and the diphenylthiocarbodiazone is removed by treatment with active charcoal. The recovered chloroform is finally distilled into 1% of its volume of ethyl alcohol.

Procedure

250 ml 0.1 *M* EDTA (disodium salt) solution, 250 ml distilled water and 50 ml NH_4OH ($d = 0.88$) were added to 1-l dithizone residues in a 2-l separating funnel. The contents of the funnel were shaken vigorously for 2 min, during which time the chloroform layer usually changed from reddish-blue to green. If the chloroform layer was still coloured reddish-blue, the alkaline EDTA solution was discarded and the above treatment was repeated. The green chloroform layer was transferred to another 2-l separating funnel and shaken for 2 min with 500 ml distilled water containing 25 ml ammonium hydroxide ($d = 0.88$). The layers were allowed to separate and the orange-yellow chloroform phase was run into a 2-l separating funnel and shaken well for 2 min with 30–40 g active charcoal. After filtration, the clear chloroform solution was distilled, the first 50–60 ml of distillate being discarded. Brown glass bottles containing 1% of their volume of ethyl alcohol (96%) were used as receivers. These were swirled several times during the distillation.

In order to test the suitability of the product, 1.0 ml of a 0.0015% dithizone solution in pure chloroform was diluted to 20 ml with the recovered chloroform. The optical density of the solution was measured at 620 mμ in a 1-cm cell. After storage in dark at ~5° for 5 days the optical density was again measured.

DISCUSSION

Chloroform recovered by the proposed method was suitable for analytical purposes; there was no change in the optical densities of dithizone solutions prepared from it after 5 days storage in the dark at ~5°. A batch of dithizone residues contaminated with phosgene gave a satisfactory product when purified by the proposed method. The time taken for the proposed method was approximately 2 hours as against 5 hours for that of MULLIN AND RILEY. Although the proposed method has only been applied to residues containing lead and zinc dithizonates, it should be applicable to other dithizonates provided they are easily dissociated and contain metals which react with EDTA.

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Thorium-EDTA complexes — A conductometric study

The disodium salt of ethylenediaminetetraacetic acid (EDTA) complexes thorium[1]. CABELL[2] studied this system potentiometrically; he indicated that in addition to the 1 : 1 complex, a 2 : 1 complex was formed and that the complex ThY_2 was less stable than ThY. This note reports a conductometric study of thorium–EDTA complexes.

Standard solutions of thorium nitrate and EDTA were prepared from AnalaR reagents. All conductivity measurements were made on a conductivity bridge (Industrial Instruments Inc., U.S.A. Model Re 216-B). An aliquot of standard thorium nitrate was placed in the conductivity cell, diluted to 15.2 ml and titrated with EDTA. A typical curve is given in Fig. 1(a). Two inflections were obtained corresponding to 1 : 1 and 1 : 2 complexes between thorium and EDTA.

The presence of two complexes was also observed when EDTA was placed in the cell and titrated with thorium nitrate. A typical curve is given in Fig. 1(b). The stoichiometric relationship between thorium and EDTA was checked by titrating different concentrations of thorium nitrate with EDTA. Table I gives the results obtained which indicate the formation of two complexes. From the shape of the curve — inflection 2 of Fig. 1(a) and inflection 1 of Fig. 1(b) — it can be seen that the higher complex was more dissociated[3]; this confirms CABELL's results.

When a mixture of thorium nitrate and EDTA in the molar ratio of 1 : 1 was titrated conductometrically with sodium hydroxide, the acid liberated corresponded to 2 equivs. of thorium. When the ratio of thorium nitrate to EDTA was 1 : 2, no acid was liberated, which indicates that the reactions are:

$$Na_2H_2Y + Th(NO_3)_4 \rightarrow ThY + 2\ HNO_3 + 2\ NaNO_3$$

$$ThY + 2\ HNO_3 + 2\ NaNO_3 + Na_2H_2Y \rightarrow H_4ThY_2 + 4\ NaNO_3.$$

This conductometric study thus confirms that 1 : 1 and 1 : 2 complexes are formed between thorium and EDTA.

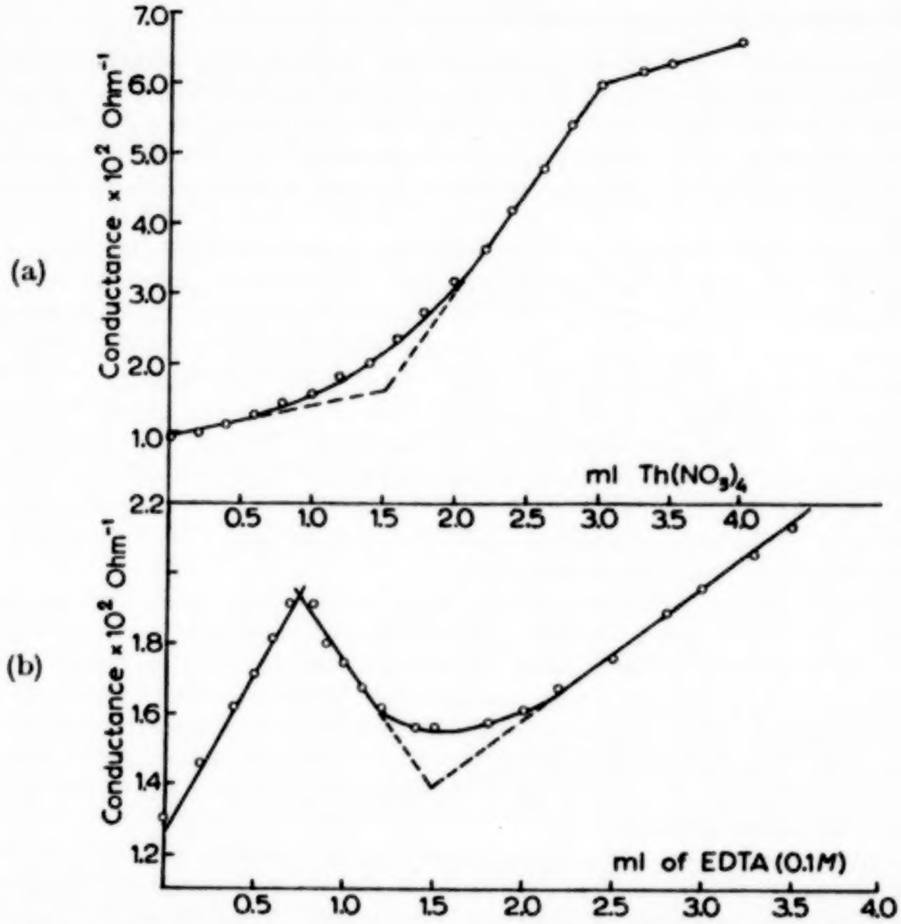

Fig. 1(a). Titration of EDTA (15.2 ml of 0.0148 *M*) with thorium nitrate (0.07511 *M* of thorium); (b) Titration of thorium nitrate (15.2 ml of 0.00494 *M* thorium) with EDTA.

TABLE I

TITRATION OF Th WITH EDTA

Th taken for titration mg	*Concentration at 1st inflection in* 10^3 *M*		*Concentration at 2nd inflection in* 10^3 *M*	
	Th	*EDTA*	*Th*	*EDTA*
4.36	1.22	1.20	1.21	2.44
8.71	2.41	2.40	2.35	4.90
17.43	4.71	4.70	4.50	8.90
26.40	6.90	6.92	6.48	12.74

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Received April 16th, 1960

REVUES DE LIVRE

Handbuch der mikrochemischen Methoden, Band 1/Teil 2, *Waagen und Wägung*, von A. A. Benedetti-Pichler. *Geräte für die anorganische Mikrogravimetrie*, von Friedrich Hecht, Springer Verlag, Vienne, 191 Abb. IV + 307 Seiten. 1959. Ganzleinen $ 19,05, bei Verpflichtung zur Abnahme des gesamten Handbuches, Ganzleinen $ 15,25.

Il y a quelque temps, nous avions le plaisir de présenter aux lecteurs des *Analytica Chimica Acta* le volume I,1 de cette série. Peu après, parut le volume II,1 et aujourd'hui nous avons entre les mains le volume I,2. Ainsi que son titre l'indique, l'ouvrage est composé de deux parties, la première concernant les balances et la pesée, la seconde, l'appareillage utilisé en microgravimétrie minérale. Il est tout à fait superflu de présenter les auteurs, tous deux étant des autorités dans le domaine de l'analyse microchimique.

La première partie, concernant les balances, comprend les chapitres suivants: *Allgemeiner Teil.* Präzision und Genauigkeit. Die Präzision der Wägungen. Die Genauigkeit der Wägung. *Präzisionshebelwaagen.* Allgemeine Beschreibung der Waage. Allgemeine Beschreibung von bei Waagen benutzten Zusatz- oder Hilfsgeräten. Theorie der gleicharmigen Hebelwaage. Beschreibung der Leistungsfähigkeit einer Präzisionshebelwaage. Aufstellen und Reinigen von Präzisionshebelwaagen. Allgemeine Ratschläge zur Behandlung von Präzisionswaagen. Wägung durch Massenvergleich. Austarieren. Neigungswägung und Eichung der Waage. Ausführung von Proportionalwägungen. Ausführung der Gauss'schen Doppelwägung. Ausführung von Substitutionswägungen. Neuerungen an mikrochemischen Waagen. *Mikrowaagen.* Das Bauen von Mikrowaagen. Die Teile der Balkenwaagen. Wägungsprinzipien und ihre Anwendung; Mikrowaagen. Literatur am Ende jedes Kapitels. Namen- und Sachverzeichnis.

Ne pouvant pas entrer davantage dans les détails, nous nous contenterons de signaler ici que tous les problèmes ayant trait à la pesée et aux microbalances sont analysés par l'auteur avec beaucoup de clarté et sur une base scientifique. Pour une fois encore, Monsieur Benedetti-Pichler a su allier la théorie à la pratique d'une manière très heureuse. Le chapitre II traite plus spécialement des balances à fléau; on y trouvera toutes les indications nécessaires pour leur installation et entretien. Quant au IIIme et dernier chapitre, il est consacré à la construction et installation des balances à fil de quartz, de même qu'à l'installation et la manipulation des autres balances microchimiques de haute sensibilité.

La seconde partie du livre, consacrée aux ustensiles servant à l'analyse microgravimétrique, est composée des chapitres suivants: *Eigenschaften der für die Mikroanalyse geeigneten Wägungsformen. Vorbereitungen zur Analyse.* Probenahme. Einwaage. Lösen und Aufschliessen. *Reagensbehälter. Rückstandbestimmungen.* Organische und anorganische Substanzen. *Fällen und Fällungsgeräte.* Fällungsgefässe. Fällen. Rühren. Mikrorückflusskühler. Einleiten, bzw. Überleiten von Gasen. Mikropipetten. Pinzetten. Tiegelzangen. *Filtration, Filtergeräte, Auswaschen.* Verfahren nach F. Emich und seiner Schule. Verfahren nach F. Pregl und seiner Schule. Filtration mittels der Zentrifuge. *Lösen und Umfällen von Niederschlägen. Trocknen der Niederschläge. Glühen der Niederschläge. Abdampfen.* Geräte. Methodisches. *Abrauchen. Methodik nach* J. Donau. *Dichtebestimmung von Flüssigkeiten.* Literatur am Ende jedes Kapitels. Namen- und Sachverzeichnis.

Monsieur Hecht avait déjà traité ce sujet dans la partie générale de son traité classique de microanalyse. Néanmoins, il ne s'agit pas ici d'une simple reprise du sujet, mais plutôt d'un travail de compilation où l'on trouvera toutes les données concernant l'emploi des différents vases, ustensiles et autres appareils microchimiques préconisés depuis la naissance de la microchimie jusqu'à nos jours. La microélectrolyse sera traitée dans un autre volume de la série, aussi ne fait-elle pas partie du livre présent.

Nous sommes heureux d'avoir entre les mains un recueil aussi complet des techniques microchimiques minérales, recueil qui épargnera à bien de chimistes des recherches fastidieuses dans le très vaste champ de la bibliographie chimique.

En concluant, nous tenons à recommander vivement cet excellent livre, persuadés qu'il rendra bien des services aux microanalystes.

I. Kapétanidis (Genève)

Anal. Chim. Acta, 23 (1960) 202

Treatise on Analytical Chemistry, (en trois parties) par I. M. Kolthoff et P. J. Elving, assistés de E. B. Sandell, 1ère partie, Vol. 1, *Théorie et pratique*, The Interscience Encyclopedia, Inc., New York, 1959, 809 pages, Prix: $ 17.50.

Ces auteurs ont entrepris une oeuvre d'envergure, celle de faire un ouvrage comprenant tous les chapitres de la chimie analytique, tant classique que moderne, tant pratique que théorique, une sorte de vaste encyclopédie. Elle comprendra trois parties ayant pour titre: théorie et pratique,

Anal. Chim. Acta, 23 (1960) 202–203

la chimie analytique des éléments, analyse des produits industriels et elle sera constituée d'un nombre important de volumes, encore non défini, semble-t-il. Le sujet est si vaste que les auteurs ont dû s'adjoindre de nombreux collaborateurs, pour le premier volume, le seul sorti de presse à ce jour, il y en a 15. C'est dire que chaque partie est traitée par un spécialiste particulièrement averti tant au point de vue théorique que pratique.

Le volume 1 comprend deux sections. La section A a pour titre général: La chimie analytique, ses objectifs, son rôle et ses limites. Les principaux chapitres sont: les méthodes de l'analyse chimique, les erreurs en analyse chimique, précision et exactitude, échantillonnage. La section B, intitulée: application des principes chimiques à l'analyse, traite des éléments et composés, du poids atomique, de l'équilibre chimique, de la représentation graphique, des potentiels d'électrodes, de la nature et de la détermination du pH, de la notion acide-base, de la force des acides et des bases et des courbes de neutralisation qui en découlent, de l'équilibre acide-base en milieu non-aqueux, de la complexométrie, du mécanisme des réactions d'oxydo-réduction, des équilibres d'oxydo-réduction et des courbes de titration, de la solubilité des précipités (formation, propriétés, pureté), des équilibres et des réactions de précipitation. Cette section n'est pas terminée, on en trouvera la suite dans le prochain volume.

Il est difficile de se faire une opinion d'un ouvrage d'une telle ampleur sur un premier volume. On peut néanmoins en tirer quelques remarques. Ce traité ne s'adresse qu'aux lecteurs ayant déjà de solides bases de chimie analytique, aux étudiants avancés, comme aux chimistes qui se destinent à l'industrie ou à la recherche pure. Ce livre va loin et profond et donne une foule de renseignements qu'on ne trouve pas dans d'autres ouvrages. C'est un vrai traité de chimie générale. Quelques chapitres sont entièrement consacrés à la physico-chimie et donnent de tels détails qu'on peut se demander s'ils ne seraient pas plus à leur place dans un livre spécialisé. Les auteurs peuvent répondre à cette objection en montrant que les phénomènes physico-chimiques sont présentés de telle sorte que les applications analytiques en découlent tout naturellement, avec une logique rigoureuse et c'est vrai pour la plus grande partie des chapitres écrits par des physico-chimistes qui ont pensé analytique.

Ce livre renferme des parties très remarquables, susceptibles d'ouvrir de nouveaux horizons; telles sont, par exemple, celles qui traitent des représentations graphiques, des équilibres acide-base où les auteurs, après CHARLOT, adoptent la théorie de BRÖNSTED, qui est certainement la mieux adaptée à la chimie analytique. Citons encore le chapitre sur la conception du pH et celui des réactions entre complexes.

Ce premier volume fait bien augurer de la suite de cet ouvrage qui deviendra, nous en sommes certains, un des outils indispensables tant au chercheur qu'au chimiste de l'industrie, de même qu'à celui qui est chargé d'enseigner les principes et les applications de la chimie analytique. Inutile de louer la présentation, le soin avec lequel les graphiques, les figures, les tableaux sont présentés. C'est la coutume des éditions américaines.

D. MONNIER (Genève)

Gas Chromatography Abstracts 1958, par C. E. H. KNAPMAN ET C. G. SCOTT, Butterworths, London, 1960, 262 p. Prix: 42 s.

Les auteurs présentent une bibliographie très complète des travaux effectués en chromatographie gazeuse jusqu'à fin 1958. Il y a 1468 références, chacune d'elles comprend le titre de l'article, le nom des auteurs et de l'ouvrage et un court résumé de 2 à 6 lignes. En outre ce livre renferme un index des auteurs et une table des matières fort bien comprise grâce à laquelle il est possible de trouver rapidement les articles parus dans un domaine particulier tel que par exemple considération théorique, appareillage, détecteur, colonnes, gaz entraineur, etc.

À l'intérieur de chacune de ces rubriques, les sujets sont classés par ordre alphabétique. Compilation intelligente et qui rendra les plus grands services à tous ceux qui ont recours à cette remarquable méthode de séparation et de dosage.

D. MONNIER (Genève)

Gmelins Handbuch der anorganischen Chemie, 8. Auflage, Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse. *Alphabetische Folge zur Systematik der Sachverhalte* (Sonderband), in deutscher und englischer Sprache, 1959, IV, 109 Seiten, Kartoniert DM 30.—, Ganzleinen DM 35.—.

Zu dem 1957 erschienenen Sonderband *Systematik der Sachverhalte* ist jetzt als Ergänzung der Sonderband *Alphabetische Folge zur Systematik der Sachverhalte* erschienen. Durch die Mitaufnahme einer grossen Anzahl von Begriffen und Synonyma, die im systematischen Teil nicht berücksichtigt waren, hat sich die Zahl der Stichworte auf etwa 5.000 erhöht. Jedes Stichwort ist mit einer Schlüsselzahl versehen, die dem seit Jahren beim Gmelin Institut bewährten System der Klassifizierung der Begriffe entspricht. Diese Schlüsselzahlen eignen sich gleichzeitig als Grundlage für automatische Dokumentationsverfahren. Der Band enthält neben dem deutschen Verzeichnis auch einen englischen Index mit den entsprechenden Schlüsselzahlen. Dieser Index dürfte besonders den auf dem Literaturgebiet tätigen Chemiker interessieren.

K. Eder (Genf)

ANNOUNCEMENT

The twelfth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Penn-Sheraton Hotel in Pittsburgh, Pennsylvania, U.S.A., from February 27 through March 3, 1961. About 150 papers will be presented on all phases of analytical chemistry and spectroscopy. A symposium entitled *New Frontiers in Optics and Spectroscopy* will be sponsored jointly by the Pittsburgh Conference and the Optical Society of America.

Original papers are invited on all phases of analytical chemistry, spectroscopy, and nucleonics applied to analysis. The final date for receipt of abstracts is October 15, 1960. Two abstracts should be submitted in triplicate. The first abstract should be limited to 150 words to be printed in the program. The second abstract should be of approximately 500 words to help the Program Committee evaluate and classify the paper. A letter sent with the abstracts should list the names of authors, laboratory in which the work was done, and the current addresses of the authors. All correspondence should be addressed to:

Dr. William F. Harris, Program Chairman of the Twelfth Annual Pittsburgh Conference,
Research Laboratories, Westinghouse Electric Corporation, Pittsburgh 35, Pennsylvania,
U.S.A.

In addition to the program of technical papers, there will be an exhibition of the newest instrumentation for analysis. More than seventy-five companies will display instruments, chemicals, and equipment.

NEW SPECIFIC ANALYTICAL PROCEDURES FOR THE DETECTION AND CHARACTERIZATION OF 1,4-NAPHTHOQUINONES

E. SAWICKI AND W. C. ELBERT

Air Pollution Engineering Research, Robert A. Taft Sanitary Engineering Center, Public Health Service, U.S. Department of Health, Education and Welfare, Cincinnati, Ohio (U.S.A.)

(Received February 1st, 1960)

INTRODUCTION

Evidence for the presence of quinones in the air has been presented in a paper introducing a thermochromic test for inner ring *p*-quinones and fluorenones[1]. Further, to assist in the detection and characterization of the various families of quinones, specific tests for terminal ring *o*- and *p*-quinones[2] and for inner ring *o*-quinones[3] have also recently been described.

Quinaldinium salts and many other active hydrogen compounds can be used to detect 1,4-naphtoquinones, but other terminal ring quinones also react[2]. Phenylhydrazines have been used for the detection of 1,4-naphthoquinones[4,5], but many other types of quinones, aromatic aldehydes and ketones give just as brilliant color reactions.

It has been reported that derivatives of 1,4-naphthoquinone give a red fluorescence when a dry spot containing this material is examined under ultraviolet light[6]. In confirmation of this, 1,4-naphthoquinone and its 2,3-dichloro-, 2-hydroxy-, 2-methyl-, 2-amino-, 2-hydroxy-4-phenylimino-, 2-anilino-3-chloro-, 2-anilino-, and 2,3-dibromo-

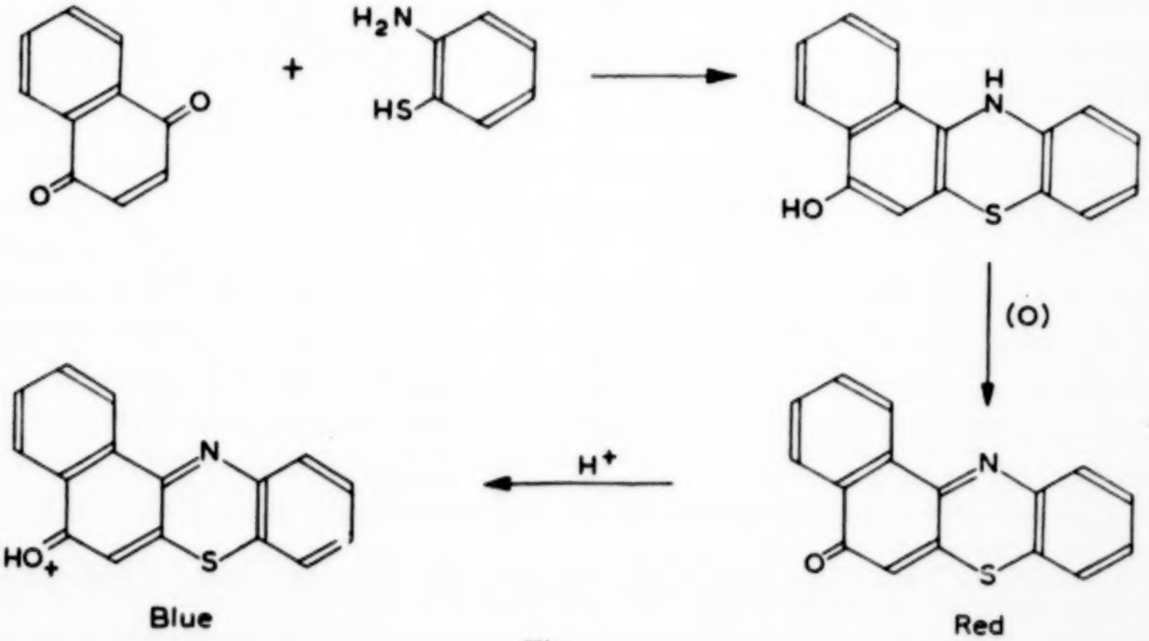

Fig. 1.

derivatives and benz[e]acephenanthrylene-9,12-dione were all found to give a dull red spot under ultraviolet light.

In this paper we would like to introduce some specific and much more sensitive methods for the detection of 2 types of 1,4-naphthoquinones.

In the first type the colorations formed in the color test probably involve the mechanism as shown in Fig. 1.

For this sequence of reactions the presence of air and acid is necessary.

As 2-hydroxy-1,4-naphthoquinone gave negative results in the terminal ring quinone tests[2] and in the present *o*-aminothiophenol test, a new method for the analysis of this compound was developed. The mechanism for the reaction is postulated as follows (see Fig. 2).

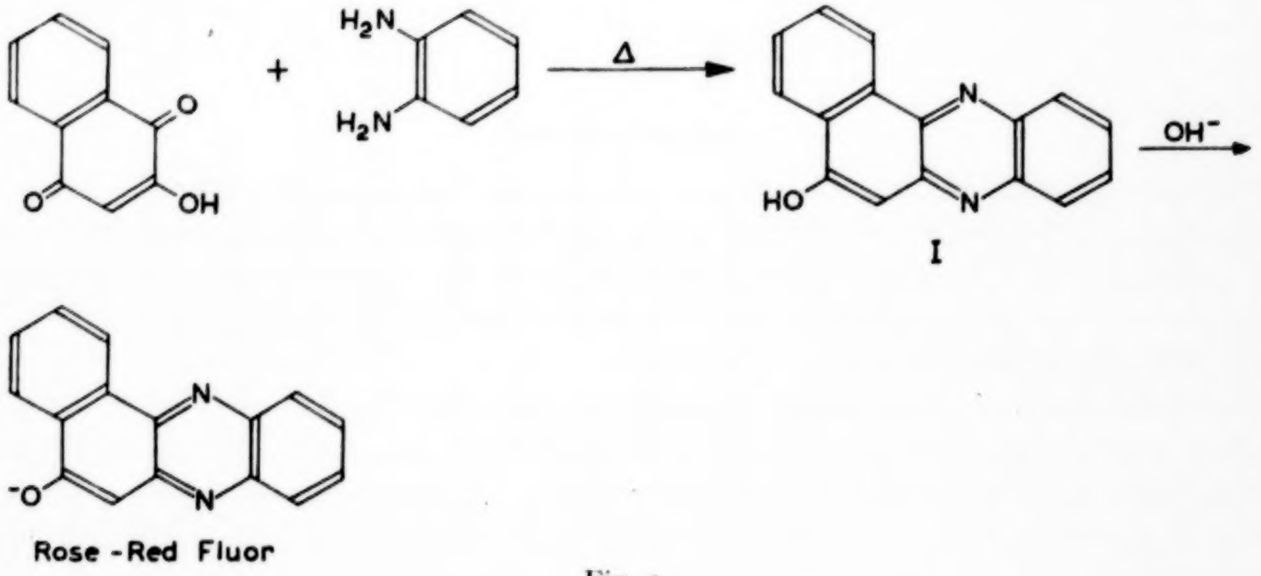

Fig. 2.

The compound, 1, was prepared by literature procedure[7] and was found to give the same striking rose-red fluorescence on paper in alkaline solution.

Color reagent

A mixture of 0.5 ml of *o*-aminothiophenol (American Cyanamid Co.) and 4 ml of concentrated hydrochloric acid was diluted to 50 ml with water. This reagent was stable for at least several days.

TABLE I

SPOT TEST FOR 1,4-NAPHTHOQUINONES

Compound	*Color*		*Ident. limit, µg*
	Base	*Cation*	
NQ[a]	Red	Blue	0.1
2-Methyl-NQ	Red	Blue[b]	0.05
2-Chloro-NQ	Red	Blue	0.01
2,3-Dichloro-NQ	Red	Blue	0.005
2,3-Dibromo-NQ	Red	Blue[c]	0.5

[a] NQ is 1,4-naphthoquinone.
[b] Steam heating the stain causes the color to change to red. However, a drop of hydrochloric acid will bring the blue color back.
[c] Unlike the other compounds, this one gave a blue ring surrounding a yellow-brown stain.

Procedure

A drop (0.03 ml) of the reagent is placed on filter paper followed by 1 μg of methanolic test solution placed in the middle of the drop. At this stage the paper can be waved in the air so as to hasten the oxidation to the red benzophenothiazone. After a 1- to 2-min waiting period, the color is noted and then a drop of concentrated hydrochloric acid is added. The color is again noted. The colors and identification limits obtained for some 1,4-naphthoquinones are presented in Table I.

Reagent for 2-hydroxy-1,4-naphthoquinone

One-half gram of *o*-phenylenediamine was dissolved in 4 ml of concentrated hydrochloric acid and 20 ml of water and then diluted to 50 ml with water. This reagent is stable for at least 1 day.

Procedure

One drop of the reagent is placed on filter paper followed by 1 μg of acetic acid test solution. The wet spot is heated with a jet of steam for 2 min. Then a drop of 10% aqueous potassium hydroxide solution is added. The paper is examined under ultraviolet light. A brilliant rose-red fluorescence denotes the presence of 2-hydroxy-1,4-naphthoquinone. The identification limit for this compound is 0.3 μg.

Remarks: In both new tests the following quinones gave negative results: benzoquinone, 2,5-dichloro-*p*-benzoquinone, 1,2-naphthoquinone, 1,2-naphthoquinone-4-sulfonic acid, phenanthraquinone, anthraquinone, and acenaphthenequinone. In addition, the following compounds also gave negative results: formaldehyde, acetaldehyde, benzaldehyde, phthalaldehyde, terephthalaldehyde, cinnamaldehyde, acrolein, acetone, benzalacetone, dibenzalacetone, anisalacetophenone, 2,4-pentanedione, benzanthrone, pyruvaldehyde, biacetyl, benzil, nitromethane, 1-octene, and 2,4-pentadiene.

In the *o*-aminothiophenol test negative results were obtained with 2-hydroxy-, 2-amino-, 2-anilino-, 2-anilino-3-chloro-, 2-hydroxy-4-phenylimino-1,4-naphthoquinones. Apparently the substitution of a fairly strong electron-donor group in the 2-position causes a negative reaction in the test. Benz[e]acephenanthrylene-9,12-dione also gave a negative result in the test.

Of the 1,4-naphthoquinones that gave positive response in the *o*-aminothiophenol test, 2-methyl-1,4-naphthoquinone was the only one which gave a blue color that faded to red on being heated with steam. Treatment with a drop of concentrated hydrochloric acid brought back the blue color. Apparently the dye formed from this quinone has a weaker basicity.

The quinones giving a positive test in the *o*-aminothiophenol procedure can be further characterized by the absorption spectra of the dyes in acid solution. For example, when 2 ml of concentrated hydrochloric acid is added to 1 ml of a methanolic solution of 1,4-naphthoquinone and 1 ml of the *o*-aminothiophenol reagent, shaken gently for 2 min and then diluted to 25 with trifluoroacetic acid, a brilliant blue solution results with wave length maxima (in the order of decreasing intensity) at 595, 772, 548, 512 (shoulder) and 700 (shoulder) mμ. The 2-methyl derivative also gave a blue color with a somewhat similar spectrum except that its long wave length band was at approximately 800 mμ. On the other hand the 2,3-dichloro- derivative gave a purple-brown color with the long wave length band at 740 mμ while the 2,3-dibromo analogue gave a band near 775 mμ.

In the *o*-phenylenediamine test all 1,4-naphthoquinones gave the dull dark red color under ultraviolet light except 2-hydroxy-1,4-naphthoquinone which gave a gleaming rose-red fluorescence. The difference between the two types of fluorescent color is striking. The brilliant rose-red fluorescence can be easily differentiated.

The dull dark red fluorescence discovered by Green may be more easily obtained by evaporating 1 μg of an acetic acid solution of a 1,4-naphthoquinone on paper and then examining the paper. Identification limits of 1 to 10 μg are thus obtained on Whatman No. 1 filter paper in a daylit room. The dull red fluorescent spots obtained for 1,4-naphthoquinone, 2-methyl-1,4-naphthoquinone, 2,3-dichloro-1,4-naphthoquinone and benz[e]acephenanthrylene-9,12-dione faded under ultraviolet light. However, if a drop of 10% aqueous potassium hydroxide solution was added to the dry spot, the red color obtained under excitation by ultraviolet light was much more stable.

SUMMARY

A new sensitive and specific color test for 1,4-naphthoquinones is introduced. With the reagent, *o*-aminothiophenol, a red color is obtained in neutral solution and a blue color in acid solution on paper. 1,4-Naphthoquinones containing electron-donor groups in the 2-position give a negative reaction. With additional spectrophotometric studies the quinones giving a positive test can be differentiated. A new specific fluorescence test for 2-hydroxy-1,4-naphthoquinone has also been developed. Reaction with *o*-phenylenediamine on paper and then treatment with alkali gives a brilliant rose-red fluorescence.

RÉSUMÉ

De nouvelles réactions sont proposées pour l'identification des naphtoquinones-1,4. Avec l'*o*-aminothiophénol, on obtient une coloration rouge, en solution neutre, et bleue, en solution acide. L'hydroxy-2-naphtoquinone-1,4 réagit avec l'*o*-phénylènediamine en donnant une fluorescence rouge rose, en milieu alcalin.

ZUSAMMENFASSUNG

1,4-Naphtochinone reagieren mit *o*-Aminothiophenol unter Bildung einer roten Färbung in neutraler Lösung und einer blauen Färbung in saurer Lösung. Hydroxy-2-naphtochinone-1,4 reagieren mit *o*-Phenylendiamin in alkalischem Milieu unter Bildung eines Reaktionsproduktes, das eine starke rosarote Fluoreszenz zeigt.

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A METHOD FOR IDENTIFYING PARTICULATE FLUORIDE COMPOUNDS*

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(Received February 18th, 1960)

INTRODUCTION

The problems arising from fluorides in the atmosphere have been discussed by those interested in air pollution and agriculture[1,2]. The fact has been established that soluble fluoride compounds in the atmosphere can cause injury to plants, and through the plants, injury to animals[3]. It seems probable that the speed of sorption of the fluorides by the plant, and thus the extent of damage, might depend not only on the solubility of the compound but the particle size, the smaller sizes being more quickly available.

These considerations made it appear desirable to devise a test which would also indicate particle size for fluoride as an atmospheric contaminant. The general method of identifying individual species among airborne particulates has already been described by LODGE[4]. The sample is collected on a membrane filter, which is floated on a reagent designed to be a precipitant for the ion of interest. The precipitant is made as selective as possible to prevent interference. When the reaction has occurred, the filter is washed by floating on distilled water, dried, made transparent with immersion oil, and examined in the optical microscope. The reactions are seen as small circular clusters of crystals at the site of each particle containing the ion in question.

EXPERIMENTAL

The reagent used was lead chloride according to the method of SCHWARZKOPF AND HEINLEIN[5]. The test depends on adjustment of lead and chloride concentrations to give a solution which is 0.057 M in lead. This may be achieved by mixing one part of 10% (w/v) sodium chloride with 3.2 parts of 10% lead nitrate. Lead chloride is precipitated and removed by centrifugation. The supernate is the reagent. In the presence of fluoride ions lead chlorofluoride is precipitated, which is sufficiently insoluble to be well suited to quantitative studies. As prepared, the solution has a pH of about 5.0. This may vary, but should not be below 4.0.

A few ml are placed in a small petri dish and the sample filter with salts of soluble fluorides is placed on the surface until the filter has been thoroughly wetted for 5 min.

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* This research was sponsored by the United States Public Health Service under Grants PHS S-12 (c2) and PHS S-12 (c3). This paper was presented at the Air Pollution Symposium in the Division of Water, Sewage and Sanitation Chemistry at the national American Chemical Society Meeting, September 1959.

It is then placed on the surface of a few ml of distilled water for 2 min, removed to a desiccator, dried and mounted. When more insoluble salts, such as fluosilicates, constitute the sample, the pH is lowered to 2.5 with acetic acid. A piece of blotting paper is soaked with the acidified reagent and the filter placed on it. The use of the blotter prevents motion of the filter and allows the reactions to form in a more compact fashion. When fluosilicates are suspected to be present, it is advisable to use a membrane filter without grid marks, as the acid reagent does not yield complete reactions around the marked lines. The fluosilicate samples react more quantitatively if the filter is first placed in a closed dish with a few drops of water and warmed very gently for half an hour. All other reaction times and procedures are the same as for soluble salts.

Insoluble fluoride-containing minerals such as cryolite and aluminum fluoride may be reacted by placing the filter on the blotter soaked with acid reagent for 1/2–1 hour. The wash on distilled water is for 3 min; the sample is dried and mounted as before. Laboratory tests show that when gaseous HF is drawn through the filter, a generalized reaction over the entire surface may be seen. After about 50 h, all the HF has diffused from the filter and the reaction no longer occurs. Therefore, samples containing HF cannot be shipped or stored but must be reacted immediately after collection. If soluble carbonates are suspected to be present, the filter must be placed in a closed dish with a few drops of HCl for one hour before reaction. This removes the carbonate but has no effect on the fluoride. Insoluble and mineral carbonates, and halides do not interfere. Sulfates and phosphates precipitate. Calcium fluoride does not react at all.

The fluoride precipitates are best seen as anisotropic white crystals in the optical microscope with crossed polars. They show polarization colors, which are especially distinctive in precipitates greater than 10 μ in diameter. The precipitates with sulfates are isotropic and extinguish completely under crossed polaroids. They may be ignored. The interference from phosphate is more serious, as it is frequently found in relation with fluorides. The precipitates are also anisotropic and visible under crossed polaroids. The distinguishing feature is their lack of polarization colors in contrast to the brilliance of the fluoride precipitate which appears to scintillate, even under reduced light, while the phosphate compound becomes fainter. Some skill with an optical microscope is required to make the identification, and practice with known compounds is advisable before heterogeneous samples are examined. Fluoride and phosphate precipitates cannot be distinguished in photographs.

Calibration

The diameters of the precipitates can be related to the diameters of the original particles[6]. This allows the sizes and mass of the original particles to be calculated. Two laboratory calibrations were made, one for soluble fluoride and one for fluosilicate. As an example of a soluble fluoride, sodium fluoride was collected on membrane filters. Similar collections of potassium fluosilicate were made for the second example. One section of the filter was examined immediately, the particles counted, and their diameters measured. A second section was reacted and the reaction sites in an equal area of the filter counted and measured. This was repeated several times to check for reproducibility. The statistical procedures involved in relating the reaction site diameter to the particle diameter, and the calculation of the geometric standard deviation have been described[6,7]. In both of these cases the reaction–particle relation was linear, though the growth was considerably greater for the sodium fluoride. This equation is $d_r = 6.8\, d_p$ with a geometric standard deviation of ± 1%, where d_r and d_p stand for diameter of reaction and diameter of particle, respectively. The equation for the calibration using potassium fluosilicate is $d_r = 1.55\, d_p + 1.25$ with a geometric standard deviation of ± 2% (Fig. 1).

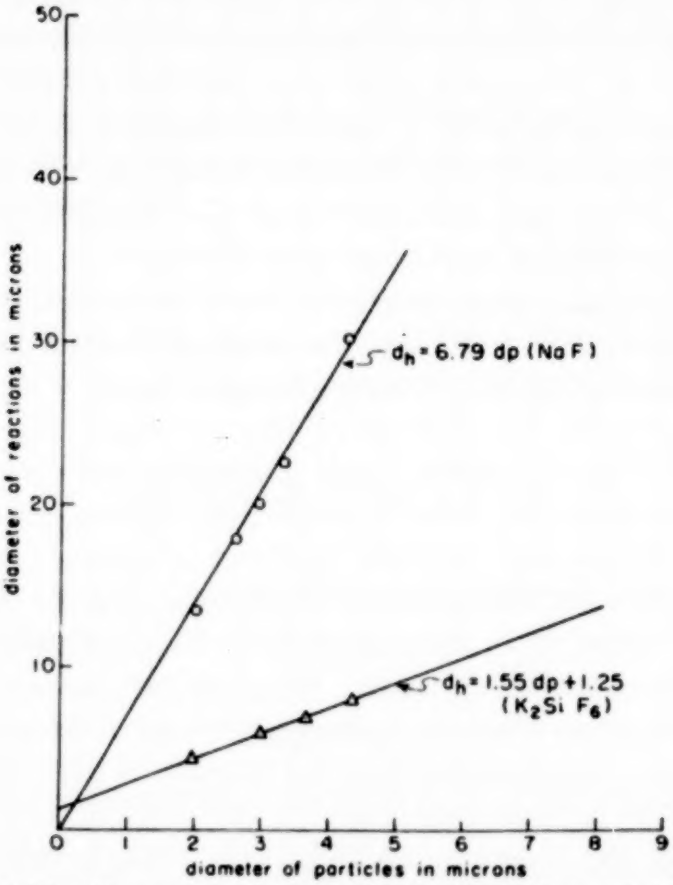

Fig. 1. Calibration curves for two typical fluoride-containing salts.

In order to find the lower limit of the test for soluble fluorides, the method was extended to the electron microscope. The sample of NaF as a test substance was collected on an electron microscope grid and reacted on a drop of reagent according to the method of TUFTS AND LODGE[8]. The grid is reacted with the sample side in contact with the reagent for 2 min and washed with the particle side away from the reagent for 1 min. Calibration was done both by measuring a series of particles and reactions from the same collection but different grids, and by measuring particles, reacting, and measuring the same reactions on the same grid. Both methods showed the calibration curve to be $d_r = 2.6\, d_p$ for NaF, with a standard deviation estimated at less than 5%.

The method is quantitative for particles having diameters at least as small as 1000 Ångstrom units.

Enlarged electron micrographs were prepared of the precipitates with fluoride, sulfate, and phosphate for close examination. The three can be distinguished by slight differences in structure. The fluoride salt is composed of tight clusters of rosettes, the sulfate precipitate has individual crystals either cubic or tetragonal in form and the phosphate has such fine structure as to appear amorphous even at high magnifications. The electron microscope method is somewhat tedious and is recommended only for special conditions where data on submicron particle sizes are desired.

Field tests

In order to test the efficiency of the method, efforts were made to take samples in the field. Simultaneous samples on membrane filters and by other standard collection methods were planned, in order to compare results. The first collections proved to be nearly totally of gaseous HF and did not survive shipment from the field site to the laboratory, suggesting that in such areas, arrangements be made for immediate reaction. The second set was obtained in an area where high particulate fluoride levels were known to occur. At the same time that the membrane filter samples were collected, samples were taken with a one cfm impinger in a Whitsell Auto-Imp sequential sampler[9]. The analysis was conducted using a perchloric acid distillation of the slightly alkaline absorption solution[10] and the distillate was titrated by the WILLIAMS method[11] as modified by ADAMS AND KOPPE[12].

The membrane filter samples were treated as described and the numbers of reactions seen counted and measured. To calculate the mass of fluoride present, the reactions were assumed to be spheres and the following formula used:

$$M = \frac{\pi}{6}\,\frac{R}{v}\,(10^{-12})\,\sum_i \left(\frac{D_{ri}}{6.8}\right)^3 N_i$$

where: D_{ri} = the reaction site diameter of the ith class, (μ), N_i = number of reactions in the ith class on the filter, R = density of NaF, V = volume of air sampled, (m^3) and the result is in grams per cubic meter. As many size classes may be chosen as is convenient; in the data given about ten classes were used. Another possible source of error in these data is the assumption that the fluoride is present as the sodium salt. This enters the calculation both in regard to the density and also, as TUFTS AND LODGE[8] have noted, in the particle–reaction ratio. Rough calculations for the case least conducive to a large particle–reaction ratio suggests that, if all the fluoride were actually ammonium fluoride, the mass value would be too high by a factor of about 3.5. Since in general atmospheric fluorides tend to be mixed, the choice of the sodium salt as representative is not unreasonable. Considerations of appearance may also influence the choice of the salt.

The comparison of the results of the particulate analyses and analyses of the impinger samples are shown in Table I. Although as stated above HF can be detected on

TABLE I

COMPARISON OF FLUORIDE SAMPLES COLLECTED ON MEMBRANE FILTERS AND IMPINGER

Sample date 1959	*Total air cu. ft.*[b]	*Total sample, MF. µg/m^3, as NaF*	*Average sample impinger µg/m^3, as HF*
7/10 – 7/14	3.09	0.012	2.8
7/14 – 7/16	3.09	0.019	8.1
7/16 – 7/17	11.58	0.0063	18.5
7/17 – 7/21	5.85	0.0033	9.2
8/11 – 8/12	220.99	0.14	[a]

[a] No data available, due to equipment failure.

[b] Samples were actually collected only during winds from northerly directions.

the membrane filters, other work has shown[13] that placing a filter in front of an impinger does not markedly change the results found when no filter is present. Therefore, these data are interpreted to mean that the largest amount of fluoride is present as the gas and the particulate comprises about 0.1% of the total. The presence of HF can only be deduced qualitatively on the filter. Due to a breakdown of the equipment, no impinger data are available for the last sample. The much higher mass is confirmed qualitatively, however, by the fact that during the period of this sample a severe fluoride pollution episode occurred.

In general, regardless of total numbers, the particle sizes were evenly distributed, showing a slight maximum in the one micron diameter range and few particles larger than 5-μ diameter, dry size.

Conclusions

The method is useful as a supplementary procedure for determining the ratio of particulate to gaseous fluoride in conditions of contamination or air pollution. Once the necessary skills with the optical microscope are acquired, the technique provides a rapid method for estimating the amounts of particulate fluoride in any given sample and distinguishing it from phosphates and sulfates present in the same sample. Because of the increase in reaction time for compounds of decreasing solubility, the procedure is readily applicable to the determination of soluble fluoride compounds most readily available physiologically.

ACKNOWLEDGEMENTS

Field samples were received through the courtesy of Polk County Air Pollution Control District, Florida, and the Air Pollution Research Laboratory, State College of Washington. Additional analyses of samples were provided by Kem-Tech Laboratories, Inc., Baton Rouge, La. Arrangements for obtaining the samples were made through Air Pollution Engineering Research, USPHS, Cincinnati, Ohio. Particle-reaction calibrations were made by U. NERI, laboratory assistant. This assistance is gratefully acknowledged.

SUMMARY

A method is described for identifying particulates containing fluorides and other complex fluorine compounds such as fluosilicate in samples collected on membrane filters. The filter is treated with lead chloride to precipitate lead chlorofluoride at each fluoride-containing spot. This microspot is identified by examination in a light microscope. Sulfate and phosphate, which also precipitate if present, can be distinguished and do not interfere. Calibrations are given for the fluorides and the more insoluble salts, relating the original particle size to the reaction site size. Thus the mass of the particles can be calculated. Results of some field tests in an area of fluoride pollution are given, and compared with standard testing procedures.

RÉSUMÉ

Une méthode est décrite pour l'identification des fluorures et des complexes fluorés dans les poussières atmosphériques, qu'on recueille sur un filtre à membrane et qu'on traite par le chlorure de plomb; le chlorofluorure de plomb formé est examiné au microscope.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Identifizierung von Fluoriden und komplexen Fluoriden in Staubteilchen. Die auf einem Membranfilter gesammelten Staubteilchen werden mit Bleichlorid behandelt und die entstandenen Flecken von Bleichlorofluorid unter dem Mikroskop untersucht.

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NEW COLORIMETRIC APPLICATIONS OF THE CHROMATE–*o*-DIANISIDINE SYSTEM

I. INDIRECT COLORIMETRIC DETERMINATION OF ANTIMONY(III), HYPOSULFITE, HYDRAZINE, HYDROXYLAMINE AND HYDROGEN PEROXIDE

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(Received February 16th, 1960)

In a previous paper[1], we have described the reaction of chromate with *o*-dianisidine to give a deep red colour; this allows the identification of chromate up to a dilution of 1 : 2,000,000 ($D = 10^{-6.3}$) and its colorimetric determination up to a dilution of 1 : 1,700,000 (0.6 μg Cr/ml).

The methods described in the present paper are based on this colour reaction, and involve the attempted indirect colorimetric determination of some inorganic reducing agents (As^{+3}, Sb^{+3}, $S_2O_3^{-2}$, $S_2O_4^{-2}$, NH_2-NH_2, NH_2OH, and H_2O_2). The general method consists of oxidizing the ion or compound with a known excess of potassium chromate; then the excess is determined by measuring the extinction of the red colour developed when the chromate reacts with *o*-dianisidine in an acidic medium. In preliminary tests, it was shown that the compounds obtained by the chromate oxidation of each of the above reducing substances had no action on *o*-dianisidine.

At the low concentrations used in the colorimetric method, the behaviour of some of these reducing substances did not always agree with the literature data. For instance, arsenic(III)[2] and sulfite[3] were not reduced by chromate at very dilute concentrations, hence their determination was not possible.

Good results were obtained for the nitrogen-containing compounds studied; hydrazine was completely oxidized to nitrogen[4,5] while hydroxylamine, whose oxidation according to the literature is not stoichiometric, several compounds, chiefly N_2O[6], being found, was also readily determined.

The method permits a simple, rapid colorimetric determination of very small amounts of the ions and compounds mentioned except for arsenic(III) and sulfite. Obviously, any other substances which are oxidized by chromate interfere in the determination.

Details of the absorption spectra between 200 and 1000 mμ of the red colour obtained at pH 1.5 and the bluish green colour at pH 3.5 are given below; the variation of the extinction and the validity of Beer's law is described in each case.

EXPERIMENTAL

The absorption spectra of the red and blue colours are shown in Fig. 1. The spectra coincide exactly with the spectra previously obtained over the range 420 to 780 mμ.

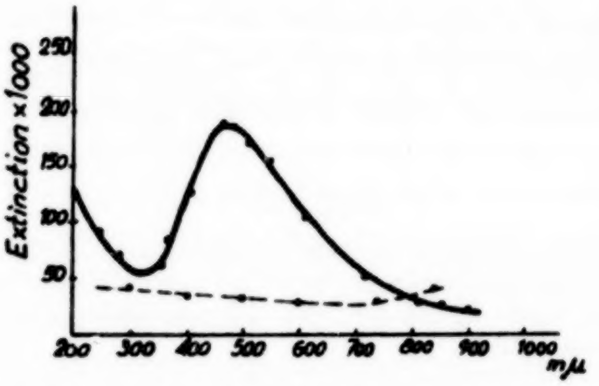

Fig. 1. Absorption spectra in the presence of substances resulting from the oxidation with chromate.
•——• at pH 1.5; – – – – at pH 3.

The interval has now been extended to cover the range between 200 and 1000 mμ as a Beckman DU spectrophotometer was available for the present work. It was found

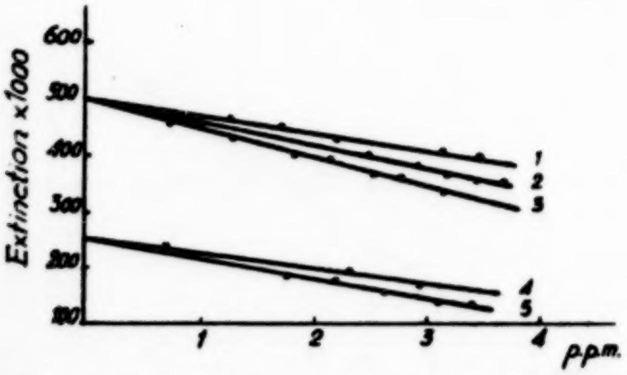

Fig. 2. Variation of the extinction with the concentration at pH 1.5 and 470 mμ. Initial chromate concentration 2 μg/ml, (1) NH_2-NH_2; (2) NH_2OH; (3) Sb^{+3}. Initial chromate concentration 1 μg/ml; (4) H_2O_2; (5) $S_2O_4^{-2}$.

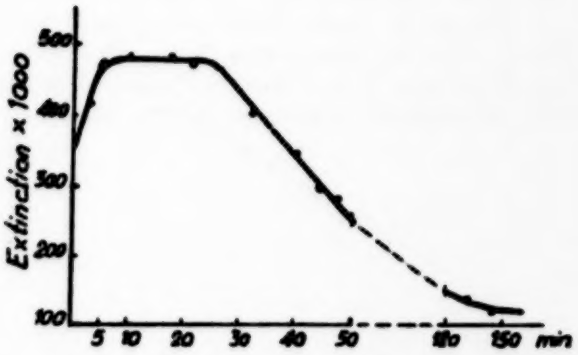

Fig. 3. Variation of the extinction with time at pH 1.5 and 470 mμ.

that the optimum wavelength was 470 mμ and the optimum pH value 1–2. The general procedure for the indirect colorimetric determinations is similar to that described previously for the determination of chromate with *o*-dianisidine[1]. The limits of validity of Beer's law for each of the compounds analysed are shown in Fig. 2. In Fig. 3 the variation of the colour extinction with time is shown; it can be seen that the values of the extinction remain constant for 25 min which is sufficient for normal usage.

PROCEDURE

2 ml of a potassium chromate solution containing 200 μg/ml are placed in a 100-ml volumetric flask. The solution containing the compound to be determined is added followed by 3 ml of 5 *N* sulfuric acid. The mixture is left for 5–10 min to ensure complete reaction, and then 0.5 ml of an *o*-dianisidine solution (0.5 g of *o*-anisidine dissolved in 50 ml of acetone and diluted to 100 ml with water) is added. The extinction is measured between 5 and 30 min after the reagent addition at a wave length of 470 mμ and with the slit suitably adjusted to attain the highest sensitivity of the spectrophotometer.

SUMMARY

New methods for the indirect colorimetric determination of antimony(III), hyposulfite, hydrazine, hydroxylamine and hydrogen peroxide, based on the colour reaction between chromate and *o*-dianisidine are described. The substance is oxidized with a known excess of chromate and the excess is determined by measuring at 470 mμ the extinction of the red complex with *o*-dianisidine at pH 1.5. The methods are simple, rapid and applicable at very low concentrations (0.1–4 μg/ml).

RÉSUMÉ

Une nouvelle méthode est décrite pour le dosage colorimétrique indirect d'antimone(III), hyposulphite, hydrazine, hydroxylamine et peroxyde d'hydrogène. Cette méthode consiste à oxyder les substances à analyser par un excès de chromate de potassium, que l'on détermine ensuite colorimétriquement par l'*o*-dianisidine.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur indirekten kolorimetrischen Bestimmung von Antimon(III), Hyposulfit, Hydrazin, Hydroxylamin und Wasserstoffperoxyd. Die zu untersuchende Substanz wird mit einem Überschuss von Kaliumchromat behandelt und dieser anschliessend mit *o*-Dianisidin kolorimetrisch bestimmt.

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NEW COLORIMETRIC APPLICATIONS OF THE CHROMATE–*o*-DIANISIDINE SYSTEM

II. INDIRECT COLORIMETRIC DETERMINATION OF SOME MERCAPTO COMPOUNDS: THIOGLYCOLIC ACID, THIOLACTIC ACID AND THIOMALIC ACID

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An indirect colorimetric method for the determination of some inorganic reducing agents by means of the chromate–*o*-dianisidine system has already been described[1]. The compound to be determined is oxidized with a known excess of potassium chromate and the excess chromate is determined colorimetrically by measuring the extinction of the red colour developed on reaction with *o*-dianisidine in an acid medium[2].

The present work is based on the same principle; the method is extended to the determination of some organic compounds that are easily oxidized by chromate; we selected some mercapto derivatives of technical value, *i.e.* thioglycolic, thiolactic and thiomalic acids and thioglycerin.

The absorption spectra of the red (at pH 1.5) and the blue (at pH 3) colors formed by the chromate–*o*-dianisidine system were studied in the presence of the substances produced by the oxidation of the mercapto compounds. The spectra are similar to those found in the determination of pure chromate with *o*-dianisidine[2]. The variation of the extinction with time is also the same as in the previous work[1].

Figs. 1 and 2 show the lower limits of validity of Beer's law (0.1–5 μg/ml); Fig. 2 gives more detail for the dilution limit area for thioglycolic acid.

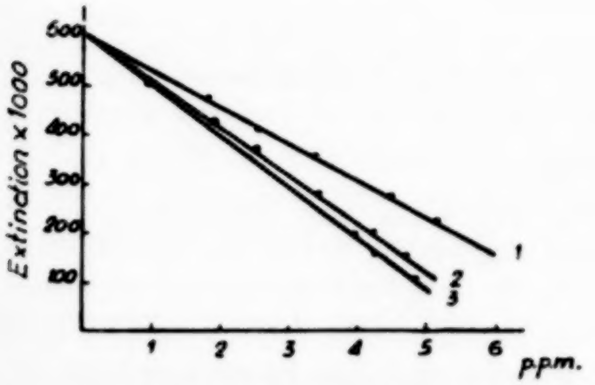

Fig. 1. Variation of the extinction with mercapto compound concentration in p.p.m. at 470 mμ and pH 1.5. (1) thiomalic acid; (2) thiolactic acid; (3) thioglycolic acid.

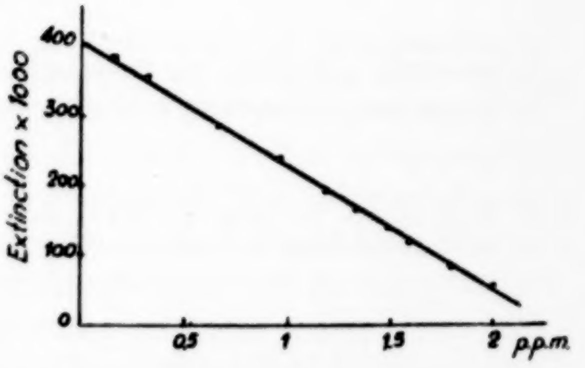

Fig. 2. Variation of the extinction in the dilution limit area; thioglycolic acid in p.p.m. at 470 mμ and pH 1.5.

This process gave good results in the determination of thioglycolic, thiolactic and thiomalic acids, but failed for thioglycerin. The procedure used is similar to that already reported[1]; the reduction of chromate by the mercapto compound also proceeds quantitatively in basic medium. One special interest of these methods is that they are the only colorimetric procedures available for the determination of thiomalic and thiolactic acids.

EXPERIMENTAL

Reagents

Potassium chromate (Analytical reagent, dried at 120°) was used to prepare a solution containing 200 mg CrO_4^{-2}/l. Mercapto compounds: all the mercapto compounds used were purified by vacuum-distillation to remove thioglycolides and other products formed by air oxidation or by intermolecular esterification: the —SH contents were titrated with iodate by the usual procedures. *o*-Dianisidine solution: 0.5 g *o*-dianisidine was dissolved in 50 ml of acetone and the volume made up to 100 ml with distilled water. Sulfuric acid and acetone: analytical grade.

Procedure

2 ml of the potassium chromate solution were placed in a 100-ml volumetric flask; the solution containing the mercapto compound is added from a microburette; an inert atmosphere should be used, in order to avoid the air oxidation of mercapto compound. This was followed by 2–3 ml of 5 N H_2SO_4 and the mixture was left for 5–10 min; 0.5 ml of the *o*-dianisidine solution was then added.

The readings were made at 470 mμ between 5 and 25 min after the colour had developed. The slit of the spectrophotometer was adjusted to obtain the highest sensitivity of the spectrophotometer.

SUMMARY

New indirect colorimetric methods for the determination of thioglycolic, thiolactic and thiomalic acids are described. The mercapto compound to be determinated is oxidised by a known excess of K_2CrO_4, this excess determinated by measuring the extinction at 470 mμ of the red colour developed when the CrO_4^{-2} reacts with *o*-dianisidine in acid medium. The method permits a very simple colorimetric determination of the mercapto compounds above mentioned, at a very low concentration (0.1–5 μg/ml).

RÉSUMÉ

De nouvelles méthodes sont décrites pour le dosage colorimétrique indirect des acides thioglycolique, thiolactique et thiomalique. La substance à analyser est oxydée par le chromate de potassium en excès, que l'on détermine au moyen de l'*o*-dianisidine.

ZUSAMMENFASSUNG

Beschreibung einer indirekten Methode zur Bestimmung von Thioglycol-, Thiomilch-, und Thioäpfelsäure. Sie beruht auf der Oxydation der Merkaptoverbindungen mit Kaliumchromat, dessen Überschuss mit *o*-Dianisidin kolorimetrisch bestimmt wird.

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THE SIMULTANEOUS DETERMINATION OF TRACES OF SELENIUM AND MERCURY IN ORGANIC COMPOUNDS BY X-RAY FLUORESCENCE

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INTRODUCTION

Many of the most efficient procedures for the introduction of unsaturation into organic compounds involve catalytic dehydrogenation with selenium dioxide[1] or selenium dioxide in the presence of mercury[2]. Since both selenium and mercury are capable of forming organo-metallic compounds, they may be carried through the subsequent reactions into the final product. The toxicity of these metals requires that they be shown to be substantially absent in products intended for oral consumption by humans and animals. Thus an accurate procedure for their quantitative determination in the p.p.m. range was necessary.

The present chemical methods for the quantitative determination of microgram quantities of selenium[3,4] and mercury[5], while extremely sensitive, are difficult to apply. An X-ray absorption method[6] gives excellent results but lacks the sensitivity required. To circumvent the necessity for destruction of the sample and conversion of the elements to a known valence state and to overcome the large sample required by the chemical methods an X-ray fluorescence procedure for the quantitative determination of selenium and mercury in the solid state has been developed. The procedure is non-destructive of the sample, rapid, and accurate.

EXPERIMENTAL

Preparation of solid samples

The samples are ground in a mortar to give a fine powder. Six hundred mg of material are weighed (± 1–2 mg) and placed in a 1.4 × 2.0 cm opening milled into a 1/8 × 1-1/4 × 1-1/2 in aluminum plate which is resting on a polished steel surface. The sample is tamped with a spatula until tightly compressed. Three thicknesses of 0.5 mm lead are placed on top of the sampie which is then compressed at 8,000 lbs/sq. in. pressure in any suitable hydraulic press. The lead is removed from the back of the sample to give a brick of compound held in an aluminum sample holder. Removal of the lead was found necessary since it contributes a large amount of scatter to the background readings.

Very finely powdered samples and/or samples with a high static charge may be tamped into the holder by the addition of small droplets of Skelly B or some other low boiling liquid in which the material is not soluble. The solvent is allowed to evaporate from the compacted sample before compression. Samples submitted as large crystals must be ground to assure the formation of a brick which will not crumble during the analysis. When properly prepared the bricks require considerable pressure to remove them from the sample holder.

Liquid samples

Materials whose selenium content and solubility permit a determination in solution are dissolved in known concentration in any suitable solvent, provided the solvent contains no heavy element (*i.e.*, halogens). The solution is added to a specially designed cell by use of a hypodermic syringe. The sample solution volume is not critical to the analysis provided the cell is full (about 2.5 ml of solution). The cell, shown in Fig. 1, is made of aluminum. The Mylar window (one mil thick) is held between the front plate and cavity block by the ten screws; no gasket is necessary to prevent leakage. Two 13-gauge hypodermic needles are used in the construction, which permits the filling and washing of the cell with a standard syringe. After the cell is filled, Teflon plugs are inserted in the needles. The cell may be temperature-controlled by the passage of water through a channel around the cell cavity.

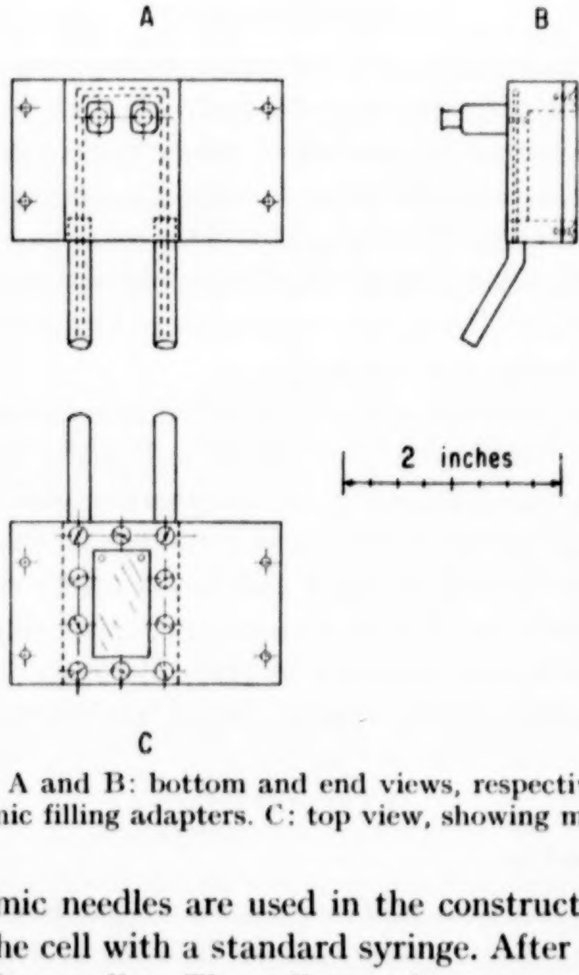

Fig. 1. Liquid sample cell. A and B: bottom and end views, respectively, showing cooling tube and hypodermic filling adapters. C: top view, showing mylar window.

Preparation of standard samples

The solid standard samples were prepared in the following manner: (Se): 3.149 mg of a seleno-steroid of known structure and purity (mol. wt. = 936.86) were dissolved in alcohol to give a solution containing 10.64 μg/ml of Se. Measured portions of this standard (or an appropriate dilution of it) were added to 3.000 ± 0.001 g of testosterone. The sample was dissolved in alcohol–acetone on a steam bath and, after the initiation of crystallization, evaporated to dryness. The dried crystals were ground in a mortar to give a finely divided powder. (Hg): Samples were prepared in an identical manner except that a solution containing 3.706 μg/ml of Hg was prepared from mercuric acetate. The liquid samples were prepared by serial dilution of a standard solution of diphenylselenium containing 235 μg/ml of Se.

Instrumental settings

A General Electric XRD-5 unit was used for the analyses. The primary radiation was from a tungsten target X-ray tube operated at 50 kV and 45 mA. A lithium fluoride analyzing crystal ($2d = 4.0269$ Å) and sodium iodide (thallium activated) scintillation counter were employed.

For the determination of mercury the $L\alpha$-line at 36.00° 2θ was used, and for selenium the $K\alpha$-line at 31.88° 2θ was used. For purposes of standardization, the intensities of these lines were related to the measured intensity of the tungsten $L\beta$-line at 37.40° 2θ.

The scaler circuit was set to record the time required for the accumulation of one million counts.

Procedure

Following a 30-minute instrumental warm-up period the sample is placed in the X-ray beam, and the time required for the accumulation of one million counts is measured when the goniometer setting is 31.88° (for selenium), 36.00° (for mercury), and 37.40° (for tungsten). The sample is then reversed in the holder 180 degrees and the procedure repeated. The two countings are averaged at each of the three 2θ settings. The actual variation between the values for the two positions of the sample nearly always falls within the limits of experimental error. The two time values thus determined for a particular goniometer setting will not be exactly equal due to inhomogeneity of the X-ray beam unless there is complete dispersion of the unknown element in the sample.

RESULTS AND DISCUSSION

The statistical accuracy of radiation counting is a function of the total number of counts, rather than the time required to accumulate them. For a more valid comparison of counting rates (intensity) then, the pre-set count, rather than the pre-set time method is used, and readings are taken from a timer which is synchronized with the scaler, and which stops automatically when the pre-set count is accumulated.

Ideally, the concentration of selenium is proportional to the intensity of the $K\alpha$-line at 3.88° 2θ, determined by

$$M/t_{(31.88^\circ)}, \text{ where } M = \text{one million counts and } t_{(31.88^\circ)} = \text{time elapsed at } 2\theta = 31.88^\circ$$

Two sources of error invalidate this: The primary radiation used to excite the sample varies somewhat from day to day, so samples run one day cannot be referred to a standard curve prepared previously, and sample surface inconsistencies cause wide variations in loss of X-ray energy due to scattering.

It was found, however, that the ratio of the intensity M/t of selenium to that of tungsten (from the X-ray tube) was a value independent of the above variables. For this reason, the concentration of selenium is found by taking the ratio of intensities:

$$\frac{I_{\mathrm{Se}}}{I_{\mathrm{W}}} = \frac{M/t_{(31.88^\circ)}}{M/t_{(37.4^\circ)}} = \frac{t_{(37.4^\circ)}}{t_{(31.88^\circ)}}$$

and the concentration of mercury from the ratio of intensities:

$$\frac{I_{\mathrm{Hg}}}{I_{\mathrm{W}}} = \frac{t_{(37.4^\circ)}}{t_{(36.0^\circ)}}$$

These intensity ratios are shown as functions of concentration of selenium and mercury, respectively, in Figs. 2 and 3.

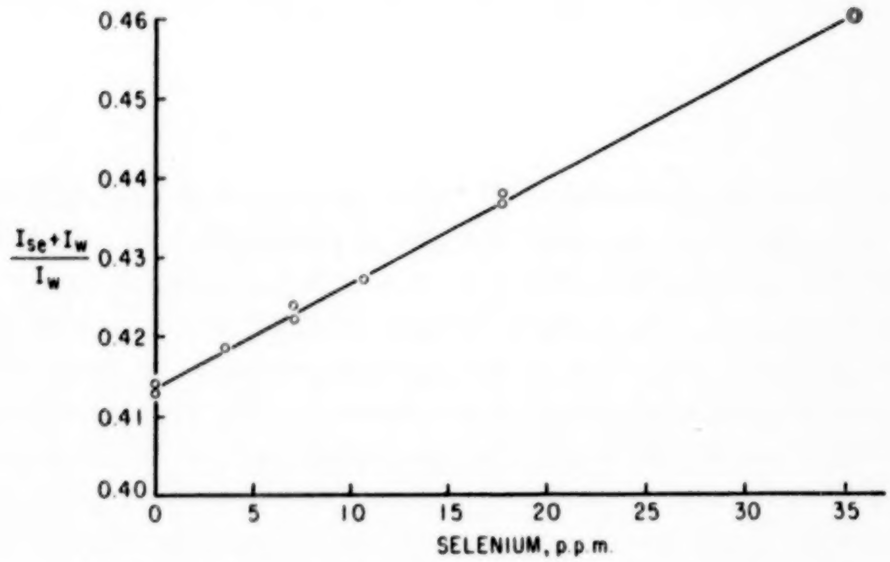

Fig. 2. Selenium, intensity ratio *vs.* concentration.

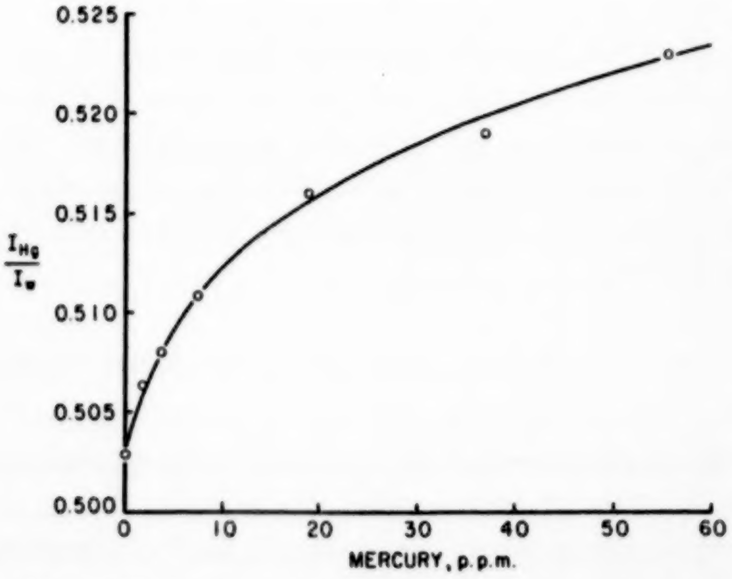

Fig. 3. Mercury, intensity ratio *vs.* concentration.

Fig. 4 shows a standard curve for the determination of selenium in solution.

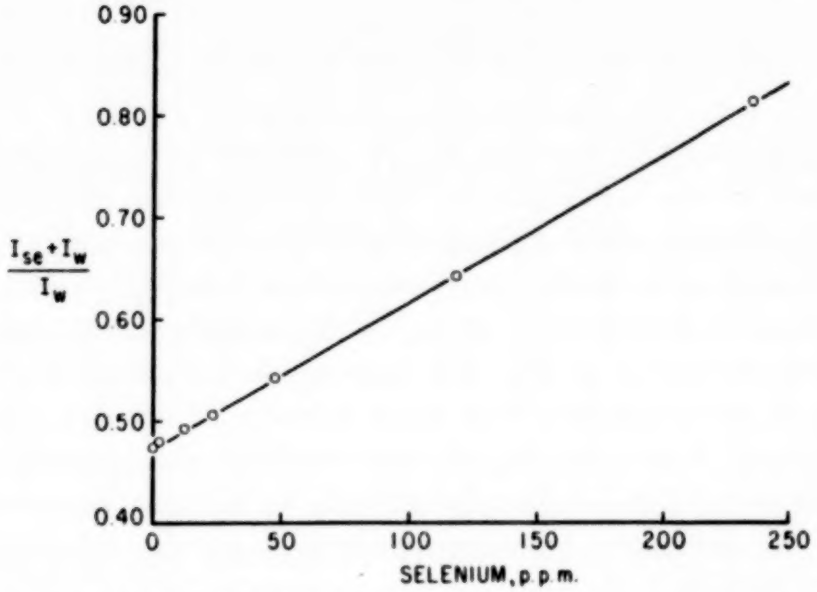

Fig. 4. Selenium in solution; intensity ratio *vs.* concentration.

Application of the method of least squares to the data from which the selenium calibration curves were drawn gives the following equations for the straight lines ($y = mx + b$) at the 95% confidence level:

Solid state (Fig. 2), $y = (0.001314 \pm 0.000036)x + (0.4134 \pm 0.0067)$;
Solution (Fig. 4), $y = (0.001442 \pm 0.000019)x + (0.4748 \pm 0.0197)$.

The curvature of the mercury plot, Fig. 3, is marked. This is expected for a heavy element in a light matrix[7]. The appearance of a straight line for selenium in Figs. 1 and 3 is explained on the basis of the occurrence of a secondary tungsten line coin-

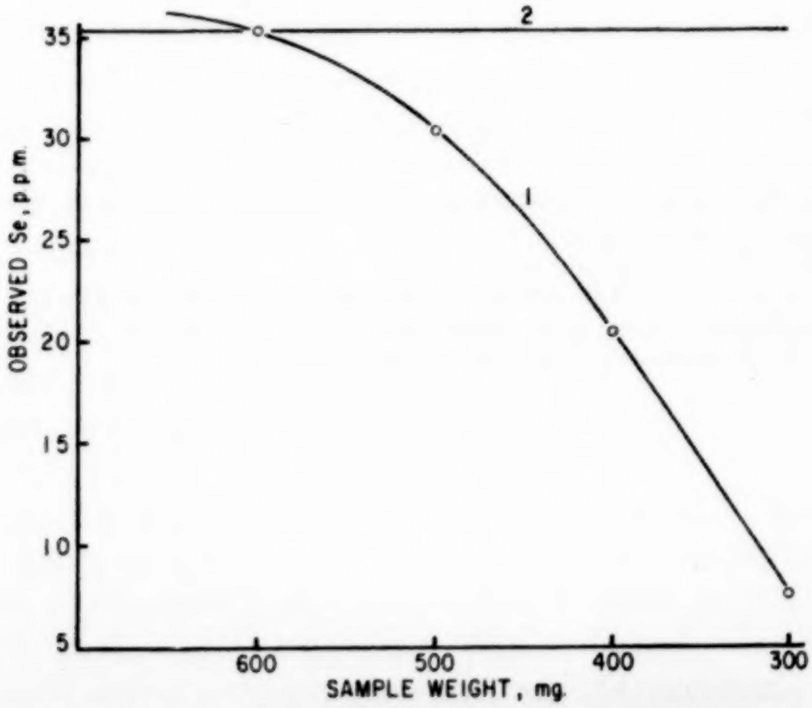

Fig. 5. Observed Se (p.p.m.) *vs.* total sample weight (mg). All samples 35.47 p.p.m. Se (theory). 1. Observed selenium, p.p.m., 2. Theoretical selenium, p.p.m.

cident with the selenium line at 31.88° 2θ. Hence, the plot is actually one of concentration *vs.* the ratio of intensities:

$$\frac{I_{\mathrm{Se}} + I_{\mathrm{w1}}}{I_{\mathrm{w2}}}$$

where I_{w1} and I_{w2} are both larger than I_{Se}. In addition selenium should be considered as a lighter element in the same matrix. This consideration alone will cause the line to straighten considerably when compared with that of mercury[7].

The effect of sample size on the analysis is shown in Fig. 5 and it is seen that in the 600-mg range the variation of ± 10 mg in the sample size introduces only a small error. By means of the curve in Fig. 5 it is possible to correct for sample size when a 600-mg sample is not available. The error introduced by this correction increases rapidly below 500 mg. Above 600 mg the curve would presumably level off as essentially infinite sample thickness was approached. No samples larger than 600 mg were prepared due to the difficulty encountered in packing them into the 1/8-inch thick sample holders.

The average time requirement for each analysis, including sample preparation, is forty-five minutes.

SUMMARY

A procedure for the simultaneous determination of selenium and mercury in organic compounds has been developed. The method, which is based upon X-ray fluorescence, gives results which are accurate to ± 1 p.p.m. in the range of 2 to 40 p.p.m. for both selenium and mercury. The procedure is rapid and is non-destructive of the sample. A 600-mg sample is required.

RÉSUMÉ

Une méthode d'analyse par rayons X proposée pour le dosage simultané du sélénium et du mercure dans des substances organiques.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur gleichzeitigen Bestimmung von Selen und Quecksilber in organischen Verbindungen. Sie beruht auf der Anwendung der Röntgenfluoreszenz Analyse.

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A SPECIFIC SPOT TEST FOR IRON

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Color reactions by phenyl-α-pyridyl ketoxime with a number of cations including ferrous iron was reported by SEN[1]. Since its first introduction, phenyl-α-pyridyl ketoximes has been employed for spectrophotometric determination of palladium and gold[2,3]. Recently TRUSSEL AND DIEHL used this reagent for the spectrophotometric determination of iron(II)[4]. In this paper a highly selective method for the detection of iron by a spot test based upon the formation of an intensely colored violet chelate of iron(II) with phenyl-α-pyridyl ketoxime is being reported.

EXPERIMENTAL

Reagent solution

A 1% solution of phenyl-α-pyridyl ketoxime*[2] in a 95% ethanol was used as reagent solution.

Procedure for the test

The test may be carried out in either of the following ways: (*a*) Place one drop of the test solution (50 μg) in the depression of a white spot plate. Add a few crystals of ascorbic acid, or hydroxylamine hydrochloride or sodium hydrosulfite followed by the addition of two drops of the reagent solution. The mixture is then made basic by the addition of two drops of 0.5 *M* sodium carbonate solution or by the addition of two drops of 6 *N* ammonia. A violet color confirms iron. (*b*) Place a drop of the test solution on a Whatman 40 filter paper. Add a drop of 10% solution of ascorbic acid and two drops of the reagent solution. Hold the wet spot over a bottle of ammonia. A violet coloration confirms iron.

Interfering ions

The following ions do not interfere with the test: Li^+, Na^+, K^+, Rb^+, Ag^+, Cs^+, Be^{+2}, Mg^{+2}, Ca^{+2}, Zn^{+2}, Sr^{+2}, Cd^{+2}, Ba^{+2}, BO_2^-, Al^{+3}, Ga^{+3}, Ce^{+3}, Tl^{+3}, CO_3^{-2}, SiO_3^{-2}, Ti^{+4}, GeO_3^{-2}, Zr^{+4}, Pb^{+2}, Th^{+4}, NH_4^+, NO_3^-, PO_4^{-3}, VO^{+2}, As^{+3}, Sb^{+3}, Bi^{+3}, $S_2O_3^{-2}$, SO_3^{-2}, SO_4^{-2}, Ca^{+2}, MoO_4^{-2}, TeO_3^{-2}, TeO_4^{-2}, WO_4^{-2}, UO_2^{+2}, VO_4^{-2}, Cl^-, Mn^{+2}, Br^-, I^-, Ni^{+2}, Ru^{+3}, Rh^{+3}, Pd^{+2}, Ir^{+4}, Pt^{+4}, acetate, oxalate, succinate, tartrate, citrate.

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* Available from G. F. Smith Chemical Co., Columbus, Ohio.

Color of the copper chelate and the color of cobalt (when the amount is more than ten times the amount of iron) chelate tend to mask the iron test. Cyanide inhibits the test.

Sensitivity

Limit of identification = 0.05 μg; dilution limit = 1 : 1,000,000.

Detection of iron in presence of copper

Detection of iron in the presence of copper can be accomplished in a number of ways. Copper may be precipitated as cuprous iodide or cuprous thiocyanate and the iron test is then performed in the usual way. Copper may also be reduced to the metallic state with sodium hydrosulfite prior to the iron test.

The test may be seen on a filter paper or a spot plate. Place a drop of the test solution on a filter paper (or in the depression of a spot plate) followed by a drop of a 10% solution of ammonium thiocyanate (or potassium iodide) and two drops of a 10% solution ascorbic acid. Add two drops of the reagent solution and hold the paper over a bottle of concentrated ammonia (or add two drops of 0.5 *M* Na_2CO_3 when spot plate is used). A violet coloration confirms the presence of iron.

The test is thus virtually free from any interference. The test may be applied for the detection of ferrous iron in the presence of ferric iron in which case no reducing agent should be used.

ACKNOWLEDGEMENT

Grateful thanks are expressed to Prof. PHILIP W. WEST for research facilities.

SUMMARY

A highly selective and sensitive spot test for iron is based on the formation of a violet colored chelate with phenyl-α-pyridyl ketoxime. The limit of identification = 0.05 μg.

RÉSUMÉ

La phényl-α-pyridylcétoxime réagit avec le fer(II) pour former un chélate violet. Cette réaction permet une identification très sélective et sensible du fer (limite d'identification 0.05 μg).

ZUSAMMENFASSUNG

Eine sehr empfindliche Tüpfelprobe auf Eisen beruht auf der Bildung eines violett gefärbten Chelates mit Phenyl-α-pyridylketoxim. Nachweisgrenze = 0.05 μg.

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A NEW METHOD FOR THE DETERMINATION OF NITRATES

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(Received February 19th, 1960)

Nitrates serve as an index of pollution in water, and oxides of nitrogen have now been recognized as one of the more important pollutants in air. The determination of nitrates up to the present has depended upon methods which are either nonspecific or nonsensitive. The present study was undertaken to investigate possible methods for the determination of nitrates that would meet the requirements common to water and air pollution studies.

The nitrate ion does not ordinarily form anionic complexes. Because of this fact and the fact that nitrate salts are so highly soluble, the determination of this ion is quite difficult. The usual reactions of nitrate are of the redox type, which makes its determination subject to a large number of interferences from other oxidants. Specific determinations involving a redox reaction with nitrate are unlikely, because the ion cannot be conveniently separated from its interferences. The method most widely used at present is the phenoldisulfonic acid method[1] which is based on the formation of a specific nitro compound. This procedure is subject to a number of interferences, the most serious being chloride ion. The method is time-consuming and difficult to perform. Also, it requires a large volume of sample, which is a distinct disadvantage. Other methods such as the nitration of 1,2,4-xylenol[2], the determination of nitrates as nitrites with the Griess reaction[3], and the reduction of nitrates to ammonia and subsequent Nesslerization of the latter[4], are subject to interferences and are all quite involved, requiring large samples and relatively lengthy preparation times.

WEST AND SARMA[5] developed a spot test for nitrate using a solution of 4,5-dihydroxy-2,7-naphthylene disulfonic acid (chromotropic acid) in concentrated sulfuric acid. The test is very sensitive and is free of common interferences. The fact that this reagent gives a yellow color which appears to vary with the nitrate concentration, and because the reaction is both sensitive and highly selective indicated that it might well be a suitable reagent for the quantitative determination of nitrates.

REAGENTS AND APPARATUS

A purified form of 4,5-dihydroxy-2,7-naphthylene disulfonic acid (disodium salt) was obtained by the addition of solid sodium sulfate to a saturated solution of Eastman practical grade salt of chromotropic acid. The salting out procedure was carried out twice to insure high purity. The purified product was then dissolved into A.R. grade concentrated sulfuric acid to give a 0.1% stock solution. The nitrate reagent was prepared by adding 1 ml of concentrated HCl to 10 ml of the stock solution and diluting to 100 ml with concentrated H_2SO_4. The solutions of the ions listed for the interference study were prepared from reagent grade salts and were free of nitrates. The interference solutions used for the study of phenoldisulfonic acid reagent were free of chlorides as well as nitrates, because the former constitute serious interferences with this particular reagent. All standard nitrate solutions were prepared by diluting proper amounts of a stock solution prepared by dissolving pure sodium nitrate in distilled water.

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A Beckman Model DK recording spectrophotometer was used to determine the wavelength at which maximum absorbance occurs. All measurements of absorbances were made with a Beckman Model B spectrophotometer which was equipped with matched quartz cells. All volumes were measured with Exax grade 10-ml volumetric flasks and volumetric pipets of 1-, 2-, and 3-ml capacities respectively.

EXPERIMENTAL

Two samples containing 5 and 30 p.p.m. respectively of nitrate ion were used to study the effect of varying acid concentrations. 2 ml of the samples were treated with varying amounts of concentrated sulfuric acid containing chromotropic acid. The mixtures were each diluted to 10 ml with distilled water, the color allowed to develop for five minutes and the absorbances then measured at 415 mμ as suggested by SARMA[5]. All absorbance values were corrected for back-ground due to the reagent. The results indicated that an initial acid concentration of 60% to 70% is sufficient for maximum color development.

A study was made of the effects of reagent concentration on absorbance measurements by investigating several concentrations of chromotropic acid in concentrated sulfuric acid. Reagent concentrations above 0.1% (w/v) gave extremely high blank backgrounds which interfered with the determination. A reagent of 0.01% gave a much lower background, high absorbance with nitrate, and results which complied with Beer's Law over concentrations of 5 to 55 p.p.m.

The wavelength at which maximum absorbance occurs is generally very critical for quantitative work. The wavelength (415 mμ) suggested earlier[5] is suitable for visual estimations for a concentration range of 5 to 50 p.p.m.; however, it was felt that this was not necessarily the optimum for trace analysis studies and an investigation was made to establish the optimum wavelength to be used to obtain maximum sensitivity.

3-ml portions of standard nitrate samples (1 through 5 p.p.m.) were treated with 7 ml of 0.01% reagent in concentrated sulfuric acid, respectively, and their absorbances run on the Beckman DK recording spectrophotometer. The results, shown in Fig. 1, indicate that maximum absorbance is obtained at 357 mμ.

The reagent-sample contact time studies indicated that two minutes contact would be sufficient for a maximum color development, and that once formed, the color remains stable for at least 96 hours.

The experiments revealed no effect of temperature on color development. The temperature studies were carried out by treating known samples of nitrate all in exactly the same way and then immersing them in a bath of boiling water for measured periods of time, diluting the sample to 10 ml, and measuring the absorbances.

A preliminary investigation of interferences indicated that the chloride ion might cause high results. A blank containing no nitrate but high chloride concentrations gave no reading, but a sample containing 1500 μg per ml of chloride and 15 μg of nitrate ion gave such a high reading that it was thought possible that increased sensitivity might be obtained by including chloride ion in the reagent and taking advantage of this effect.

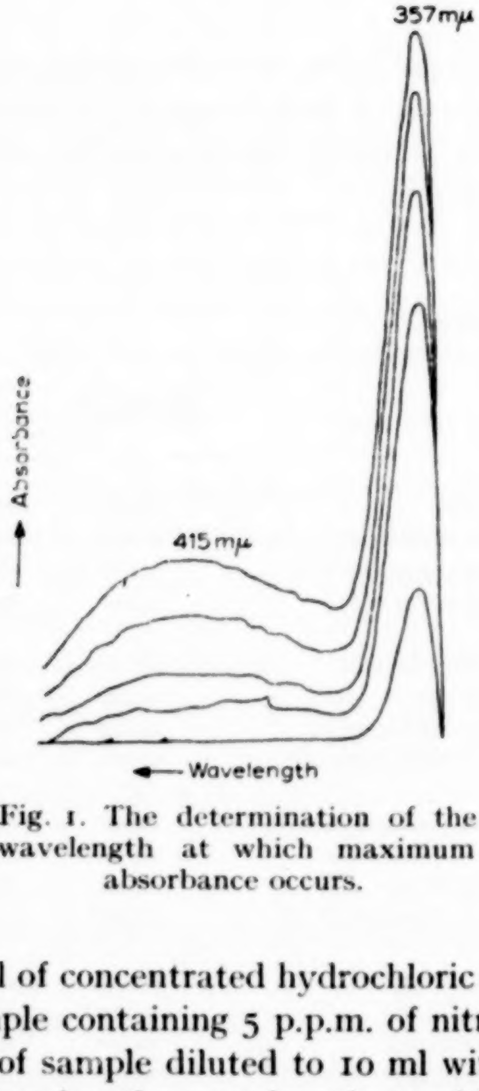

Fig. 1. The determination of the wavelength at which maximum absorbance occurs.

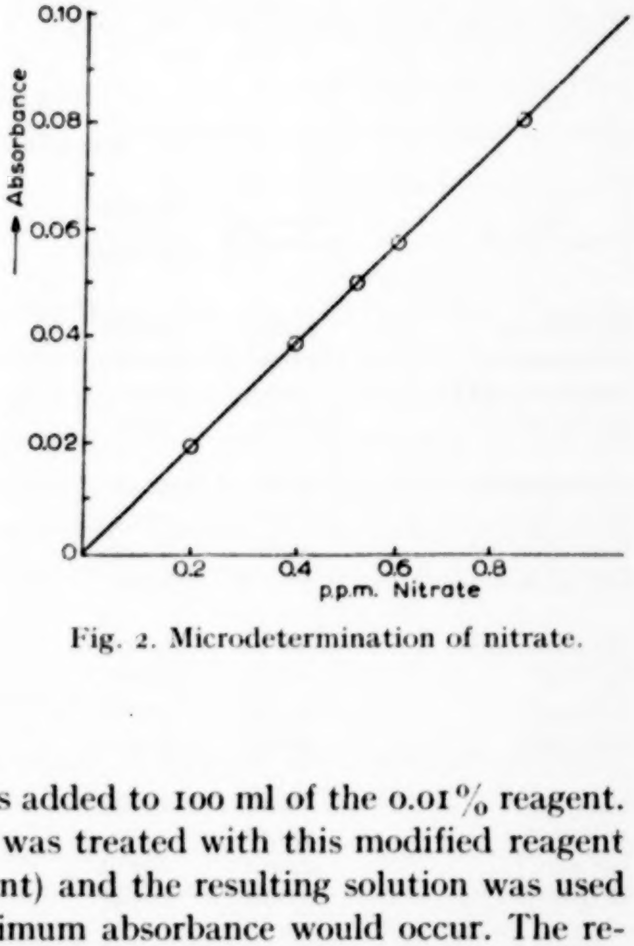

Fig. 2. Microdetermination of nitrate.

1 ml of concentrated hydrochloric acid was added to 100 ml of the 0.01% reagent. A sample containing 5 p.p.m. of nitrate ion was treated with this modified reagent (3 ml of sample diluted to 10 ml with reagent) and the resulting solution was used to determine the wavelength at which maximum absorbance would occur. The resulting plot from the Beckman DK recording spectrophotometer indicated that there was no shift in wavelength due to the addition of the chloride ion. The new reagent containing the chloride ion was then used to test a series of standard nitrate samples ranging from 1 to 5 μg per ml of nitrate ion and was found to give excellent sensitivity.

The results shown in Table I, even though not strictly linear, are quite suitable for quantitative work. It was realized immediately from these results that it should be possible to determine much smaller quantities of nitrate ion using a reagent solution containing chloride. Standard nitrate solutions were prepared for the range of 0.2 to 1.0 p.p.m. nitrate ion. 3 ml of these samples were placed in 10-ml volumetric flasks and treated by diluting up to the mark with the modified reagent. A contact time of 30 min was used so as to allow the mixture to cool to room temperature prior to measurement. The results of the absorbance measurements are plotted in Fig. 2.

TABLE I

Nitrate concentration (p.p.m.)	*Absorbance (357 $m\mu$)*	
	With added chloride	*Without chloride*
1.0	0.208	0.065
2.0	0.438	0.133
3.0	0.618	0.214
4.0	0.710	0.325
5.0	0.760	0.400

It is of interest to note that a discontinuity exists in the working curve. At low concentrations (up to approximately 1 p.p.m. of nitrate) a linear response is obtained, but above this a distinct displacement of the curve occurs so that a separate working graph must be prepared for the range of 1 to 10 p.p.m.

TABLE II

INTERFERENCE STUDIES

Ions investigated	*Chromotropic acid method*	*Phenoldisulfonic acid method*	*Ions investigated*	*Chromotropic acid method*	*Phenoldisulfonic acid method*
aluminum	none	slight	lead	none	none
ammonium	none	none	magnesium	none	none
antimony(III)	none	none	manganese(II)	none	slight
antimony(V)	none	none	mercury(II)	none	none
arsenic(III)	none	none	molybdate	10 : 1	none
arsenic(V)	none	none	nickel	none	none
barium	none	none	palladium(II)	none	none
beryllium	50 : 1	none	perchlorate	none	none
bismuth(III)	50 : 1	none	*m*-phosphate	none	none
borate	none	none	*o*-phosphate	none	none
bromate	great	great	platinum(IV)	none	none
bromide	great	great	ruthenium(III)	slight	slight
cadmium	none	none	selenate	none	none
calcium	none	none	selenite	none	none
cerium(III)	none	slight	sodium	none	none
cerium(IV)	none	none	sulfate	none	none
chromium(III)	none	great	sulfite	none	none
chromium(VI)	none	great	tellurium	none	none
chlorate	great	great	tin(II)	none	none
chloride	none	great	tin(IV)	none	none
cobalt(VI)	none	none	titanium(III)	great	none
copper(II)	none	great	titanium(IV)	great	none
fluoride	none	none	tungstate	none	none
iodate	30 : 1	none	vanadium(II)	none	none
iodide	slight	great	vanadium(V)	none	none
iron(II)	50 : 1	none	uranate	none	none
iron(III)	10 : 1	10 : 1	uranyl	none	none
gold(III)	none	great	zinc	none	none
			zirconium	none	none

Interference studies

A ratio of 1 : 100 nitrate ion to interference ion was used as a standard in an attempt to determine which ions would cause interference with determination of nitrates. A control sample and the sample containing the ion under investigation for interference were compared with an interference blank. Absorbances were measured at 357 mμ, and the results obtained on the control and interference samples were compared. If the two readings differed by more than 10%, the ion was listed as an interference. The results are listed in Table II.

RECOMMENDED PROCEDURES

Water analysis

Pipet 3 ml of the sample into a 10-ml volumetric flask. Fill the flask to the mark with 0.01% purified chromotropic acid in concentrated sulfuric acid with chloride ion added as described above. Allow the mixture to cool to room temperature, dilute to the mark, and measure the absorbance at 357 mμ. The concentrations may then be determined from a standard calibration curve, constructed by plotting known concentrations *versus* their absorbances.

Air analysis

Collect the air sample (20 l minimum) directly into 7 ml of 0.01% purified chromotropic acid in concentrated sulfuric acid with chloride ion added. Transfer the reagent-sample mixture to a 10-ml volumetric flask and fill to the mark with distilled water. Allow the mixture to cool to room temperature and measure the absorbance at 357 mμ. The concentrations may then be determined from a standard calibration curve.

Separate curves should be used for concentration ranges of 0.0 to 0.8 p.p.m. and from 1.0 to 5.0 p.p.m. nitrate ion. If the sample contains more than 5 p.p.m. nitrate, it should be diluted.

CONCLUSIONS

Prior to this work, the quantitative determination of nitrates depended on a method which is not sensitive to trace quantities of nitrate ion. The method, employing phenoldisulfonic acid, required 100 μg or more of nitrates present in the sample in order to produce sufficient color to be measured with reasonable accuracy. Samples containing one p.p.m. nitrate ion, or less, required the use of large volumes of sample with consequent tedious evaporation and associated errors. Using the phenoldisulfonic acid method, the extent of evaporation is extremely critical, the temperature of the evaporated sample prior to treatment is highly important, and the amount of mixing of the sample with the reagent is very critical. Perhaps the most serious disadvantage of the phenoldisulfonic method for the determination of nitrates is the fact that chlorides are a very significant interference. If the test is not preceded by a precipitation of chloride ion with silver ion, the color may fail to develop when even small amounts of chloride are present. Since chloride ions are probably commonly present in the majority of the samples, this is an extremely serious drawback. Even after the silver sulfate treatment, care must be exercised in order to be completely sure that all of the chlorides have been precipitated and that the silver chloride has been removed from suspension. This of course requires the tedium of filtration. All of these factors contribute to error in measurements and impose delays in the completion of a determination.

Nitrates, as a result of this study, may now be rapidly and accurately determined on samples as small as 3 ml. The procedure does not involve time-consuming evaporations which might produce losses of sample; instead it is rapid, straightforward, and simple to perform. It is truly a microdetermination involving the use of a very small portion of an often precious sample. The method has no serious interferences, especially when applied to water analysis, and it should be readily adapted to the determination of nitrogen dioxide in air, where it would be virtually free from all interfering substances. Chlorides, rather than interfering with the method, actually enhance the determination and are included in the nitrate reagent. Nitrites interfere quantitatively; however, this interference can be overcome by the addition of sulfanilic acid[5].

Phenoldisulfonic acid, which is similar to chromotropic acid, is known to react with nitrates producing a yellow tripotassium salt of nitrophenoldisulfonic acid. The high concentration of sulfuric acid involved in the new methods produces suitable conditions for nitration. Because of this and the similarity to phenoldisulfonic acid, a nitro derivative of the chromotropic acid is believed to be formed. This belief is also supported by the fact that few of the oxidizing agents interfere with this method.

SUMMARY

A new method for the spectrophotometric determination of nitrate is proposed based on the use of chromotropic acid. The method is highly selective, very sensitive, and can be quickly and easily applied. Of special significance is the lack of chloride interference (a serious restriction to the classic phenoldisulfonic acid method) and the freedom from the tedium of evaporation of samples.

RÉSUMÉ

Une nouvelle méthode sensible, sélective, simple et rapide est proposée pour le dosage spectrophotométrique des nitrates. Elle est basée sur la réaction obtenue avec l'acide chromotropique

ZUSAMMENFASSUNG

Beschreibung einer einfachen und genauen spektrophotometrischen Schnellmethode zur Bestimmung von Nitraten mit Hilfe von Chromotropsäure.

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DETERMINATION OF MAGNESIUM AND ALUMINIUM IN ZINC-BASED DIE CASTING ALLOYS

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INTRODUCTION

For the estimation of calcium and magnesium in milk JENNESS[1] used the titration with disodium ethylenediaminetetraacetate (EDTA), eliminating the interference of phosphate by removing it with the aid of anion-exchange technique. HAHN, BACKER AND BACKER[2] also applied an ion-exchange resin for the removal of phosphoric acid from cations. While JENNESS used Duolite A-4, and HAHN, BACKER AND BACKER used Amberlite IRA-400, the anion-exchange resin Dowex 1 × 8 was used in the present work. The interference of phosphate ions in the determination of magnesium may be attributed to the precipitation of magnesium ammonium phosphate when the pH of the solution is raised to 8–10, the range recommended for the titration with EDTA. FLASCHKA AND HOLASEK[3] titrated magnesium without removing phosphoric acid as did HOLTZ[4].

Recently, REILLEY AND SCHMID[5] proposed a theory of end-point detection in complexometry, with particular reference to the estimation of magnesium; they proved that the pH is an important variable in end-point detection and that the pH should indeed be between 8 and 10 for the magnesium–EDTA reaction. To obtain this pH, JENNESS used a buffer containing sodium hydroxide. The ammonia–ammonium chloride buffer of SCHWARZENBACH[6] gives better pH control. The indicator solution of JENNESS, suggested by BETZ AND NOLL[7], proved to be satisfactory and stable on storage, in contrast to most other Eriochrome indicator solutions. Another satisfactory indicator is methyl thymol blue[8]; it was confirmed that this solution was stable for about a fortnight.

The separation of magnesium ions by Dowex 1 × 8 is accomplished by simple percolation. The following points must be noted: (1) the resin should be well regenerated and washed, and free from air bubbles, (2) the solution of $MgNH_4PO_4 \cdot 6\,H_2O$ in hydrochloric acid should be prepared with a minimum of acid.

In the usual method of precipitating aluminium as aluminium hydroxide from a solution which contains mainly zinc, even after four reprecipitations the precipitate contains too much zinc to be weighed as aluminium oxide. With the particular method of precipitation described below, two successive precipitations suffice, if they are carried out in the cold by adding the solution which contains zinc to the ammonia-containing solution; this procedure may be called an inverse cold precipitation. The cold, slightly acidic zinc solution mixed with ammonium nitrate is poured into a cold solution of ammonia containing ammonium nitrate; the latter solution contains a small excess of ammonia, so that the final pH does not appreciably exceed 8 (it is usually 8.4). When the zinc solution is poured into the ammonia solution with stirring, the zinc ions present are always surrounded by an excess of ammonium ions. The following reactions may occur:

$$Zn^{+2} + 2\,NH_3 + 2\,H_2O \rightleftharpoons Zn(OH)_2 + 2\,NH_4^+$$
$$Zn(OH)_2 + 6\,NH_3 \rightleftharpoons [Zn(NH_3)_6](OH)_2$$

The quantity of ammonia used agrees approximately with the stoichiometrically calculated amount[9,11]. It is interesting to observe that the zinc which was occluded in the precipitated aluminium hydroxide as an ammine hydroxide, was partly volatilised on ignition in a platinum crucible. A grey colour appeared on the inside of the crucible which increased in weight, as is seen after removal of the aluminium oxide with molten potassium bisulfate ($K_2S_2O_7$). As zinc oxide is not volatile, we consider that the zinc volatilised as metal, formed by reduction of the zinc-containing compound with ammonia.

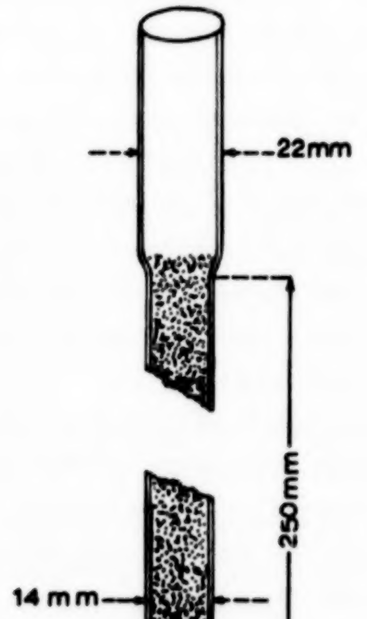

Fig. 1. Ion-exchange column.

Apparatus and reagents

A tube with approximately 20 ml of the anion-exchange resin Dowex 1 X 8,50–100 mesh (*cf.* Fig. 1). All reagents were of analytical grade. Hydrochloric acid, $d = 1.19$, idem 0.5 N. Nitric acid,

$d = 1.4$. Tartaric acid, ammonium nitrate, diammonium hydrogen phosphate, sodium acetate. Ammonia, $d = 0.91$. EDTA, Eriochrome Black T indicator: 1 g dissolved in 30 ml of water and 1 ml of 1 N sodium carbonate and diluted to 100 ml with isopropanol. Methyl thymol blue indicator: 0.1% solution in water. Buffer of SCHWARZENBACH: 70 g of ammonium chloride is dissolved in 640 ml of ammonia ($d = 0.91$).

PROCEDURES

(*A*) *Determination of aluminium*

5 g of turnings or drillings of the alloy, from which iron was removed by a magnet, were dissolved in a mixture of 20 ml of nitric acid and 80 ml of water. Nitrous fumes were boiled out. About 5 g of ammonium nitrate and 2 ml of sulfuric acid (1 : 1) were added and the solution was electrolysed to remove copper and lead, which were determined separately. The electrolysate was poured into a 500-ml volumetric flask and diluted to the mark. Of this solution 100 ml (1 g of sample) were used for the gravimetric determination of aluminium and another 100 ml for the colorimetric determination of iron.

For the determination of aluminium, 20 ml of a 50% ammonium nitrate solution were added, and the solution was neutralized to pH 3 with ammonia using congo indicator paper (to a violet colour). If the solution did not remain clear, some drops of nitric acid were added. The solution in beaker (1) was then cooled and poured, with stirring, into another beaker (2) containing 75 ml of water, 20 ml of 50% ammonium nitrate solution and 10 ml of ammonia. Beaker (1) was washed with a dilute (*ca.* 10%) solution of ammonium nitrate, acidified with 3-4 drops of nitric acid per 100 ml. The mixture in beaker (2) was then heated to about 80°. If the temperature is much higher, ammonia evaporates and zinc may contaminate the aluminium precipitate. The precipitate was then filtered through an S. & S. White (or Whatman No. 40) paper, which had been moistened with wash liquid (20 ml of 50% ammonium nitrate solution and 3-4 drops of ammonia per 100 ml), and washed with this wash liquid. It was then dissolved in warm acid (100 ml of 2 : 3 hydrochloric acid or 105 ml of 1 : 2 nitric acid). The washed filter paper was ignited and weighed to check whether the precipitate had been properly removed.

The second precipitation was performed by the addition of about 35 ml of ammonia to neutralize the acid to pH 3. Precipitation was then carried out as before after cooling but this time 8 instead of 10 ml of ammonia were added to beaker (2). In this case, the precipitate was quantitatively transferred (with pieces of filter paper) to the filter. The filter with the precipitate was then dried, ignited in a quartz crucible and weighed.

Note: By fusing the aluminium oxide with 100 times its weight of potassium bisulfate and dissolving the melt in water and 10 ml of hydrochloric acid, any occluded zinc could be determined. After addition of 4 g of tartaric acid, the solution was heated to about 80° and an excess of 5-10 ml of ammonia was added; silica originating from the quartz crucible was filtered off and 10 ml of a 7.5% solution of thioacetamide were added. The solution was heated to about 100° and allowed to cool for 2 hours. The FeS + ZnS could then be filtered and weighed as oxides. When the quantity of iron oxide (Fe_2O_3) present was obtained from the colorimetrically determined iron, any zinc oxide present in the aluminium oxide could be calculated; the percentage of zinc in the aluminium oxide after two precipitations was never more than 0.1%.

(*B*) *Determination of magnesium*

10 g of turnings or drillings of the alloy, from which iron was removed by a magnet, were dissolved in a covered 600-ml beaker in 40 ml of hydrochloric acid and 60 ml of water. Any copper present was dissolved by adding nitric acid dropwise (about 20 to 30 drops) and heating. The nitrous fumes were boiled out. After cooling 4 g of tartaric acid were added and dissolved by stirring. The solution was then diluted to 250 ml and neutralized with about 15 ml of ammonia; another 90 ml of ammonia was then added to obtain a clear solution. After cooling to about 10° (or 20°), 4 g of diammonium phosphate were added (if desired as a filtered solution). The solution was stirred until crystals of $MgNH_4PO_4 \cdot 6\ H_2O$ appeared and then left for 4 h with occasional stirring, or left overnight. The crystals were filtered off on a porcelain filter crucible (Berlin 3A2) and washed with dilute ammonia (8 ml of ammonia in 92 ml of water), and the suction funnel was cleared of some condensed copper-ammine salts. The precipitate in the beaker was then dissolved in 8–9 ml of warm 0.5 *N* hydrochloric acid and about 10 ml of warm water; this solution was passed through the crucible containing the $MgNH_4PO_4 \cdot 6\ H_2O$ and collected in a clean beaker. The 600-ml beaker and the crucible were washed with water.

Note: Stoichiometrically 12 mg of magnesium as $MgNH_4PO_4$ require 6 ml of 0.5 *N* HCl.

The capacity of the ion-exchange resin Dowex 1 × 8 for phosphate ions is about twice as great as that given by the supplier* for chloride.

The slightly acid solution of magnesium ammonium phosphate (*i.e.* $MgCl_2$, NH_4Cl, H_3PO_4 and HCl partially as ions) was then cooled and passed through the ion-exchange column, which was washed with water. The effluent was evaporated (in an Erlenmeyer flask with a boiling tube to prevent bumping) to about 25 ml and cooled. Then 3 ml of Schwarzenbach buffer, 3 ml of ammonia (2 drops per ml of the solution) and 3 drops of indicator solution were added and the solution was titrated with 0.02 *N* EDTA which had been standardised against magnesium metal or ignited magnesium oxide. With Eriochrome Black T the colour change was from violet to blue and with the methyl thymol blue from blue to grey; with the latter indicator a grey background was advisable so that the colour change was from blue to colourless.

Regeneration of Dowex 1 × 8

For regeneration of Duolite A-4 see[1], for Amberlite IRA-400 see[2]. Regeneration was necessary for each determination. Following JENNESS, we used the resin in the acetate form and regenerated with 1 *N* sodium acetate. The pH of this solution was 7.8 as measured with Lyphan-paper L 671 with a range of 7.5–8.7. Percolation of 1 *N* sodium acetate was continued until the pH of the effluent was 7.8; 70–80 ml of solution per 20 ml of resin was required. The resin was then washed with water until the pH of the effluent and the wash water were equal, *i.e.* approx. 5. Usually about 50 ml of water were required.

Maintenance of the ion-exchange column

When the column became clogged, the running time (normally 4 ml/min) increased. The contents of the column were then transferred to a beaker with water and the resin–water mixture was shaken and decanted to remove fine particles and waste; the resin was then returned to the column, not allowing the water to fall below the top of the resin.

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* ± 0.1 mequiv./g dry resin.

RESULTS AND DISCUSSION

The suggested procedure was checked in different ways: (*A*) By analysing synthetic samples, which were prepared by suitable dissolution of pure zinc, aluminium, copper and magnesium metals and by mixing these solutions. (*B*) By comparison of the results with those obtained by reprecipitation of the magnesium as $MgNH_4PO_4 \cdot 6\ H_2O$, followed by ignition and weighing as $Mg_2P_2O_7$. (*C*) By analysis of samples of known composition. The error caused by the coprecipitation of iron as hydrated ferric oxide with the aluminium hydroxide can be allowed for; the precentage of iron amounts to 0.015% at the most. The error caused by occlusion of zinc which is weighed as zinc oxide with the aluminium oxide does not vary much and is unimportant, as

TABLE I

SYNTHETIC SAMPLES ANALYSED FOR MAGNESIUM

Added mg Mg	*Added % Mg*	*Found after one precipitation*		*Found after reprecipitation*	
		mg Mg	*% Mg*	*mg Mg*	*% Mg*
3.57	0.036	4.02	0.040	3.70	0.037
5.00	0.050	6.00	0.060	—	—
7.15	0.072	7.90	0.079	7.24	0.072
10.00	0.100	10.87	0.109	—	—
15.00	0.150	15.25	0.153	—	—
0.00	0.000	0.15	0.015	—	—
0.00	0.000	0.11	0.011	—	—

Obviously a trace of zinc was precipitated in the last two cases; this coprecipitation was more obvious when the $MgNH_4PO_4 \cdot 6\ H_2O$ was examined after one precipitation.

TABLE II

SYNTHETIC SAMPLE ANALYSED FOR ALUMINIUM

Added mg Al	*Added % Al*	*Found after inverse, cold reprecipitation as described*		*Surplus Al_2O_3 ($ZnO + Fe_2O_3 +$ ash of filters) mg Al*	*Found after correction % Al*
		mg Al	*% Al*		
41.86	4.18	42.97	4.29	1.11	4.18

TABLE III

DETERMINATION OF MAGNESIUM IN ZINC-BASED DIE CASTING ALLOYS BY THE PROPOSED METHOD

Sample No.	*Found after one precipitation*		*Found after reprecipitation*		*Surplus, found after one precipitation*	
	mg Mg	*% Mg*	*mg Mg*	*% Mg*	*mg Mg*	*% Mg*
1	4.2	0.042	3.5	0.035	0.7	0.007
2	4.0	0.040	3.3	0.033	0.7	0.007
3	3.7	0.037	3.3	0.033	0.5	0.005
4	7.6	0.076	6.8	0.068	0.8	0.008
4	7.4	0.074	—	—	—	—
4*	—	—	6.9	0.069	—	—

* Gravimetric determination as $Mg_2P_2O_7$.

TABLE IV

SURPLUS FOUND IN THE ESTIMATION OF Al VIA Al_2O_3, CONTAINING OCCLUDED ZnO AND Fe_2O_3, BY DETERMINATION OF THESE IMPURITIES

Sample No.	*Al_2O_3 + Fe_2O_3 + ZnO mg*	*Fe_2O_3 + ZnO (Surplus) mg*	*% Al calculated from impure Al_2O_3*	*% Al calculated from pure Al_2O_3*
1	72.9	2.3	3.85	3.73
2	75.0	2.4	3.97	3.84
3	68.7	1.8	3.63	3.51
4	80.5	2.1	4.25	4.13
5	75.2	1.6	3.98	3.89
6	77.0	2.1	4.07	3.96
7	75.0	3.3	3.97	3.79
8	76.8	2.3	4.06	3.94
9	71.4	1.0	3.78	3.72
10	77.8	1.5	4.10	4.02
11	77.9	1.4	4.11	4.04
12	77.0	2.1	4.05	3.94

can be seen in Table IV. The amount of impurity in the aluminium oxide has a mean deviation of 0.44 and a standard deviation of 0.58.

The results for magnesium (see Tables I and III) showed that it is advisable to subtract 0.5 mg of magnesium from the amount found with one precipitation of $MgNH_4PO_4 \cdot 6H_2O$ to obtain the correct magnesium content. This means that on the average 0.5 mg of zinc are coprecipitated in the first precipitation of magnesium ammonium phosphate hexahydrate. The correct value of magnesium would be obtained by reprecipitation. The method described above has proved to be satisfactory in production control. It is a reliable substitute for the spectrographic method of magnesium determination.

Two types of methyl thymol blue are obtainable; that sold by B.D.H. is an acid–base indicator and is not suitable for this application. The recommended metallochromic indicator is obtainable from Chemapol, Prague, Czechoslovakia (as was kindly indicated by Prof. PŘIBIL to the writer).

Specific properties of the indicators

With the Eriochrome Black T indicator solution, it is advisable to clean the flask after each titration with boiling 1 : 1 hydrochloric acid. The proper course of the titration is affected by residues of the indicator which adhere to the glass. When the titration flask is only rinsed with water, the change of colour with excess of EDTA occurs prematurely, but rapidly disappears; this happens with each addition of EDTA, so that it is very difficult to find the true end-point. With MTB, the colour change becomes indistinct when the indicator solution is kept for more than a fortnight; the solution must be stored in a dark flask in a cool place.

The determinations of magnesium and aluminium described above are simple and reproducible. When magnesium ammonium phosphate is precipitated, lead should be eliminated beforehand, but copper does not interfere. Manganese and calcium also interfere.

When ammonia solution not produced from gaseous ammonia is used, the precipitate of magnesium ammonium phosphate contains some organic matter, which when ignited forms carbon in the magnesium pyrophosphate; the carbon remains occluded in the pyrophosphate as it is very refractory in this form. The original organic matter in the $MgNH_4PO_4 \cdot 6\ H_2O$ causes trouble in subsequent filtrations, hence it is advisable to clean the porcelain filter crucible in warm aqua regia and to anneal it in an electric furnace to red heat.

The method described is also advantageous for determining magnesium in aluminium alloys. SERGEANT[10] determined magnesium in aluminium alloys after either removing or complexing all the impurities which interfere in the titration of magnesium with EDTA. We modified and shortened this method; the main constituent (aluminium) was eliminated by dissolving the alloy in sodium hydroxide, and the remaining Al + Fe + Mn was removed with ammonia and ammonium persulfate before the determination was completed as described above. All glassware must be thoroughly rinsed and in special cases boiled with hydrochloric acid, to avoid the introduction of elements which consume EDTA.

SUMMARY

A titrimetric determination of magnesium in die casting alloys is described; it is unaffected by impurities commonly present in such alloys. The visual titration with EDTA is carried out after removal of phosphoric acid with an anion-exchange resin. The aluminium present in the alloy is determined gravimetrically by a special precipitation method.

RÉSUMÉ

Une méthode est proposée pour le dosage titrimétrique du magnésium dans des alliages de zinc. Le titrage est effectué au moyen de l'éthylènediaminotétracétate disodique. Un dosage gravimétrique de l'aluminium est également décrit.

ZUSAMMENFASSUNG

Beschreibung einer komplexometrischen Bestimmung von Magnesium in Zinklegierungen. Die Titration erfolgt mit Äethylendiaminotetraessigsäure (EDTA) nach Entfernung des Phosphates mit einem Ionen-Austauscherharz. Vorhandenes Aluminium wird gravimetrisch bestimmt.

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DETERMINATION OF METAL IONS BY MEANS OF TAA AND EDTA

III. DETERMINATION OF IRON

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INTRODUCTION

We have already shown[1,2] that thioacetamide (TAA) as precipitating agent and ethylenediaminetetraacetic acid (EDTA) as masking agent considerably improve sulfide and hydroxide separations of metal ions in solution. Methods for the determination of a metal of the second group (copper)[2] and a metal precipitating as the sulfide in the third group (zinc)[1] have been described. In the present paper the determination of iron is described as representative of metals precipitating in the third group as hydroxides.

As can be seen in Tables I and II of the Part I of this series[1], it should be possible to separate iron from the group II elements by precipitation of the latter as sulfides in acid medium. After neutralisation of the centrifugate with hydroxide, EDTA is added and the solution is buffered at a pH of 10 or 11. The hydroxides of aluminium, iron and manganese can then be precipitated by adding calcium chloride (demasking agent), while cobalt, nickel and zinc remain in solution. The hydroxides can be dissolved in hydrochloric acid and the iron content measured by the spectrophotometric method described by SCHNEIDER AND JANKO[3]. Aluminium and manganese do not interfere. Obviously it should therefore be possible to determine iron by this procedure, in presence of all the other elements under consideration.

The spectrophotometric method

SCHNEIDER AND JANKO added an excess of EDTA to an iron(III) solution to form a yellow complex which is oxidised with an excess of hydrogen peroxide in ammoniacal solution. A violet solution of a Fe(III)–EDTA–H_2O_2 complex, having a maximum absorption at 525 mμ, is formed. We obtained a molecular extinction of 520 at this wavelength and confirmed that Beer's law is valid within the usual concentration limits (in a Unicam SP 500 spectrophotometer). The final colour develops rapidly and is not affected by an excess of the reagents within certain limits. The following precautions have to be taken.

1. A large excess of hydrogen peroxide often causes the formation of tiny gas bubbles, which interfere with the spectrophotometric determination; 3 ml of 30% peroxide is sufficient and does not interfere.

2. The colour is photosensitive. SCHNEIDER AND JANKO do not mention this effect.

When the colours are not measured immediately it is necessary, especially on sunny days, to place the flasks in the dark directly after dilution.

3. The colour intensity depends on the temperature, but ordinary changes in room temperature have a negligible effect.

The value of 520 for the molecular extinction of the coloured complex at 525 mμ is very suitable for the present purpose. When the colour is developed in 50- or 100-ml volumetric flasks and 1- or 4-cm cells are used for the extinction measurements, 0.15–5 mg iron can be determined.

EXPERIMENTAL

*Procedure**

The determinations are carried out in 15-ml centrifuge tubes. Add to 5 ml of the solution, containing 0.15–5 mg iron, 2 to 4 drops of 36% hydrochloric acid and 4 drops of 6% TAA solution. Heat the tubes by hanging them in a water bath for 15–30 minutes, until the precipitate coagulates. Filter the precipitate (of the group II sulfides) through a G4-glass filter stick into another centrifuge tube, as shown in Fig. 1 of Part I[1]. Wash three times with 1 ml of water and remove the wash water in the same way. Replace the centrifuge tube with the solution in the water bath and heat to decompose the excess of TAA and to drive out hydrogen sulfide. Cool and add 0.5 ml of saturated bromine water to oxidize all the iron present to iron(III). Reheat in the bath to remove the excess of bromine.

Cool and neutralize the solution with 20% potassium hydroxide solution (if a precipitate appears, dissolve in a minimum of hydrochloric acid).

Add 1 ml of 0.1 *M* EDTA. If nickel and especially cobalt is present in quantities of more than about 2.5 mg, add an extra ml of EDTA for every 0.1 mmole of these metals (see Table III). If chromium is present, the solution must be heated for 30 min in a water bath at 90° to form the extremely stable Cr(III)–EDTA complex. Cool and add 1 ml of ammonia–ammonium chloride buffer solution (pH 10 or 11). Add 1 ml of 0.3 *M* calcium chloride solution to precipitate the hydroxides of iron, manganese and aluminium. Heat the centrifuge tube for 30 min in a water bath at 95° (the solution must not boil) and finally for 10 min at 100°. Centrifuge and wash twice with a slightly ammoniacal ammonium chloride solution. The supernatant liquid can be discarded, because it contains no precipitated iron hydroxide; the precipitate remains quantitatively on the bottom of the centrifuge tube.

Dissolve the iron hydroxide in a few drops of 10 *N* HCl. If manganese and aluminium are present, the tube must be heated in a glycerol bath (105°) for complete dissolution.

Transfer the solution quantitatively to a 100-ml volumetric flask (in the case of 0.15 and 0.30 mg iron, a 50-ml flask was used) and develop the colour in the following way. Add 8–10 ml of 0.1 *M* EDTA and 3 ml of 25% ammonia. Shake the solution and add 3 ml of 30% H_2O_2. Dilute to the mark with water and measure the extinction at 525 mμ.

RESULTS

Determinations in presence of other group III elements

Two series of results were obtained, one with the buffer pH 10 and the other with the buffer pH 11 solution.

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* All reagents used were of analytical grade.

(*a*) *Results with buffer pH 10*

When iron was the only group III element present, the results of the determination were usually 2–3% low. Obviously not all the iron was demasked by the addition of calcium chloride solution. This was proved by the addition of hydrogen peroxide to the supernatant liquid, when the characteristic purple colour of the Fe(III)–EDTA–H_2O_2 complex appeared. When, however, other group III elements were present, the results were usually much better; the results of some of these determinations are given in Table I.

TABLE I

DETERMINATION OF 1.50 mg OF IRON IN PRESENCE OF OTHER GROUP III ELEMENTS (pH 10)

Other group III elements present in mg						*Fe present in mg*	*Fe found in mg*	*Error in %*
Zn	*Mn*	*Ni*	*Co*	*Cr*	*Al*			
1.5						1.50	1.48	− 1.3
3							1.50	0
15							1.48	− 1.3
	2.5						1.48	− 1.3
	2.5						1.47	− 2
		2.5					1.50	0
		6					1.50	0
			2.5				1.53	+ 2
			6				1.52	+ 1.3
3			2.5				1.51	+ 0.7
3	2.5						1.50	0
3		2.5	2.5				1.50	0
	2.5	2.5					1.50	0
	2.5		2.5				1.49	− 0.7
				2.5		1.50	1.50	0
				2.5			1.50	0
				5			1.51	+ 0.7
				5			1.56	+ 4
				8			[a]	
3				2.5			1.50	0
	2.5			2.5			1.50	0
		2.5		2.5			1.53	+ 2
			2.5	2.5			1.59	+ 6
					0.5		1.44	− 4
					1.5		1.44	− 4
					1.5		1.33	−11

[a] In this experiment $Cr(OH)_3$ precipitated with iron.

The following conclusions can be drawn from Table I.

1. Aluminium interfered under these conditions. Obviously part of the iron remained in solution.

2. With only one other of the group III elements present, the results for the iron determination increased slightly in the order Zn-Mn-Ni-Co. This can be explained as follows:

a. When only zinc was present the results were low for the same reason as when no other group III elements were present;

b. for manganese the same reason as for aluminium could be valid;

c. when cobalt and nickel were present, the precipitation of iron was still not complete, but a small amount of cobalt or nickel was coprecipitated. These two elements both gave complexes with EDTA and peroxide which absorbed light at 525 mμ. For nickel the absorption was small, hence approximately correct results were obtained for the iron determinations. Cobalt absorbed strongly at 525 mμ and the results for iron were high. It was therefore necessary to add extra EDTA when nickel and cobalt were present, approximately in equivalence with the interfering element, in order to keep these metals completely in solution. A larger excess of EDTA should be avoided, because it could keep part of the iron in solution.

3. Chromium did not interfere provided that not more than 5 mg was present. Above this concentration chromium precipitated with iron as hydroxide and interfered with the spectrophotometric determination. However, addition of extra EDTA was not effective, because the large excess required to keep chromium in solution inevitably dissolved part of the iron. If iron had to be determined in presence of much chromium, this could be done by decreasing the amount of iron (see Table III).

4. If chromium was present together with nickel and cobalt high results were obtained. This can be accounted for in the same way as under *2c*.

All these difficulties vanished completely when the experiments were carried out at pH 11 because of the slow decomposition of the complex $Fe(OH)_2Y^{-3}$ (H_4Y being the symbol for EDTA) which begins at pH 10.5.

TABLE II

DETERMINATION OF 1.500 mg OF IRON IN PRESENCE OF OTHER GROUP III ELEMENTS (pH 11)

Other group III elements present in mg						*Fe present mg*	*Fe found mg*	*Error*
Zn	*Mn*	*Ni*	*Co*	*Cr*	*Al*			*%*
					1.5	1.500	1.478	−1.5
					1.5		1.490	−0.7
					1.5		1.490	−0.7
3		2.5	2.5				1.500	0
3	2.5		2.5				1.494	−0.4
	2.5			2.5	2.5		1.484	−1.0
				2.5	2.5		1.503	+0.2
				2.5	2.5		1.491	−0.6
			2.5	2.5			1.473	−1.8
			2.5	2.5	2.5		1.495	−0.3
		2.5		2.5			1.477	−1.5
		2.5		2.5			1.500	0

(*b*) *Results with buffer pH 11*

In Table II some results of determinations at pH 11 are given. To avoid bumping of these solutions buffered at pH 11, the centrifuge tubes should not be placed in a water bath at 100°. The best temperature in this case was 95°.

As can be seen in Table II, the results were much better than those at pH 10. At pH 11 the results were quite consistent and independent of the other elements present. Even aluminium no longer interfered. When iron was the only group III element present good results were also obtained (see Table IV).

Determinations of very small amounts of iron were also carried out at pH 11. Some of the results are given in Table III.

TABLE III

DETERMINATION OF 0.300 AND 0.150 mg OF IRON IN PRESENCE OF OTHER GROUP III ELEMENTS (pH 11)

Other group III elements present in mg						*Fe present mg*	*Fe found mg*	*Error %*
Zn	*Mn*	*Ni*	*Co*	*Cr*	*Al*			
0.6	0.6	0.6	0.6			0.300	0.310	+3
1.2		1.2					0.300	0
	2.5		2.5				0.303	+1
	2.5	2.5					0.300	0
	5						0.297	−1
	7.5						0.300	0
		7.5					0.300	0
	2.5		5.0				0.318	+6[a]
			7.5				0.318	+6[a]
			7.5				0.300	0[b]
					2.5	0.300	0.303	+1
					2.5		0.300	0
					7.5		0.290	−3
				2.5			0.296	−1
0.15	0.15	0.15	0.15	0.15	0.15		0.297	−1
0.1	0.1	0.1	0.1	0.1	0.1	0.150	0.149	−0.5
0.1	0.1	0.1	0.1	0.1	0.1	0.150	0.150	0
0.1	0.1	0.1	0.1	0.1	0.1	0.150	0.145	−3
				4		0.150	0.147	−2

[a] No extra EDTA was added in this experiment.

[b] Extra EDTA, equivalent to the quantity of cobalt present, was added.

The following remarks should be noted with regard to Table III.

1. If more than 2.5 mg of cobalt was present, extra EDTA was added to prevent coprecipitation of traces of cobalt.

2. Iron could be determined in presence of a large amount of chromium, provided that not more than 5 mg of chromium was present (see the last experiment of Table III).

3. If the amount of aluminium present was more than fifteen times the amount of iron, the results of the determinations were low.

Determination of iron in presence of copper

Copper was the only element of the second group which interfered with the spectrophotometric determination of iron, hence some determinations of iron were carried out in presence of this element by the given procedure. The results are given in Table IV.

TABLE IV

DETERMINATION OF 1.5 mg OF IRON IN PRESENCE OF COPPER (pH 11)

Cu present in mg	*Fe present in mg*	*Fe found in mg*	*Error in %*
1.5	1.500	1.494	−0.4
1.5	1.500	1.509	+0.6
3	1.500	1.497	−0.2
3	1.500	1.475	−1.5

Determination of iron in some alloys

The procedure was applied to two alloys.

a. Alloy containing about 80% Cu, 10% Al, 5% Ni, 4.5% Fe and 1% Mn. By the present method, the mean of 6 determinations was 4.52% with a corresponding standard deviation of the mean of 0.015%.

Analysis of the same alloy according to an ASTM procedure[4] gave 4.53%. This volumetric procedure, however, required more time and much more sample.

b. Chromium–nickel steel of the National Bureau of Standards (101 d), containing 18.67% Cr, 9.05% Ni, a few traces of other elements and 71.0% Fe.

The mean of 5 determinations was 70.7% with a corresponding standard deviation of 0.18%.

DISCUSSION

The method described for the determination of iron is quite generally applicable. Some anions that give precipitates with calcium ions in ammoniacal solution and that interfere with the complex formation of iron and EDTA, *e.g.* phosphate, oxalate and fluoride, should not be present.

In the absence of group II elements, the reduction of reducible anions, *e.g.* chromate, should not be omitted. This is done by carrying out the TAA part of the procedure, or perhaps in some simpler way.

This procedure of determining iron is simple and, as all the work is carried out in centrifuge tubes, little time is required for the total analysis. If only group III elements are present, a determination takes between one and two hours if chromium is absent and two hours if it is present. If group II elements are also present an additional hour is required. It is obvious that six or more determinations can be carried out simultaneously.

SUMMARY

Iron (0.15–5 mg) is determined in presence of group II and group III elements by precipitating group II elements as sulfides with TAA in hydrochloric acid medium, adding EDTA to the filtrate, buffering at pH 11, and precipitating ferric hydroxide by addition of calcium chloride. Iron is finally determined spectrophotometrically as the Fe(III)–EDTA–H_2O_2 complex.

RÉSUMÉ

Une méthode est proposée pour le dosage du fer, en présence des éléments des groupes II et III. Les éléments du deuxième groupe sont précipités à l'état de sulfures par addition de TAA. Au filtrat, on ajoute EDTA et on tamponne à pH 11; le fer est précipité ensuite comme hydroxyde, par addition d'une solution de chlorure de calcium. Le précipité obtenu est dissous et le fer est finalement dosé par spectrophotométrie, sous forme de Fe(III)–EDTA–H_2O_2.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Eisen in Gegenwart der Elemente der II. und III. Gruppe. Die Elemente der II. Gruppe werden als Sulfide abgetrennt und im Filtrat das Eisen als Hydroxyd gefällt. Zum Schluss wird das Eisen als Fe(III)–EDTA–H_2O_2 Komplex spektrophotometrisch bestimmt.

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SEPARATION OF NIOBIUM, TANTALUM, TITANIUM AND ZIRCONIUM FROM EACH OTHER

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The separation of niobium, tantalum, titanium and zirconium from each other is difficult because their analytical behaviour is very similar owing to their atomic volumes, ionic and covalent radii. The reactions of zirconium are somewhat different, but when associated with the other three metals, its chemical character prevents an easy separation. SCHOELLER'S[1] procedure is time-consuming, the selenious acid method[2] permits the separation of niobium and tantalum together from titanium but not from zirconium, while oxine[3] distributes titanium in the fractions of both niobium and tantalum. Pyrogallol[4], however, precipitates both niobium and tantalum and leaves titanium and zirconium in solution.

The three reagents, N-benzoyl-N-phenyl hydroxylamine[5], cinnamyl hydroxamic acid and N-cinnamoyl-N-phenyl hydroxylamine[6], which have been utilised by the authors for the determination of niobium and tantalum, also precipitate titanium and zirconium. Even rigorous pH control and the use sequestering agents such as hydrogen peroxide, oxalic, tartaric and citric acids, EDTA, salicylic acid and ascorbic acid fail to prevent precipitation. The problem can be solved as follows: both niobium and tantalum are precipitated by the pyrogallol method[4], leaving titanium and zirconium in solution as pyrogallol complexes. From the residue, niobium and tantalum are recovered by the N-benzoyl-N-phenyl hydroxylamine method[5]. From the solution, pyrogallol is first removed by digestion with perchloric acid and then zirconium and titanium are determined by the salicylhydroxamic acid[7] and the cupferron[8] methods respectively.

EXPERIMENTAL

The chemicals, reagents and standard solutions used were the same as described earlier[5-8]. B.D.H. indicator papers were used for all pH measurements.

Procedure

Aliquots of standard solutions of niobium, tantalum, titanium and zirconium were mixed and diluted to about 300 ml. Sufficient strong sulphuric acid to make its concentration between 5 and 10% (v/v) was added. All four elements were then precipitated at room temperature by the addition with stirring of an excess of N-benzoyl-N-phenyl hydroxylamine solution; the precipitate was filtered, washed with warm water and ignited in a silica crucible. The ignited mass was then fused with potassium bisulphate and extracted with about 200 ml of 5% pyrogallol solution. The solution was just neutralised with aqueous ammonia, treated with 15 ml of concentrated hydrochloric acid, digested on a boiling water bath for about 15 min and then left to stand overnight; niobium and tantalum separated as a flaky sediment. The precipitate was filtered, washed with 1% pyrogallol solution, dried and ignited. The ignited residue was again fused with potassium bisulphate and the whole procedure was repeated to free niobium and tantalum from titanium and zirconium. The mixed oxides of niobium and tantalum were then separated by the N-benzoyl-N-phenyl hydroxylamine method[5].

The filtrates and washings containing titanium and zirconium were mixed, evaporated nearly to dryness, and digested first with fuming nitric acid and then with a mixture of perchloric and sulphuric acids, in order to decompose the organic matter completely. After fuming, the solution was cooled, and diluted with water to give an acid strength of 5%. Sufficient hydrogen peroxide (20 vol.) was then added and zirconium was precipitated and determined by the salicylhydroxamic acid procedure[7]. From the zirconium filtrate, titanium was recovered by precipitation with cupferron[8] after hydrogen peroxide had been decomposed by boiling. Typical results are shown in Table I.

TABLE I

Taken, mg				*Found, mg*			
TiO_2	*ZrO_2*	*Nb_2O_5*	*Ta_2O_5*	*TiO_2*	*ZrO_2*	*Nb_2O_5*	*Ta_2O_5*
10.6	11.2	12.5	11.7	10.5	11.0	12.6	11.7
21.2	22.4	25.0	23.4	21.0	22.3	25.2	23.3
42.4	44.8	50.0	46.8	86.9[a]		97.2[b]	
31.8	33.6	50.0	46.8	65.2[a]		97.0[b]	
42.4	44.8	12.5	11.7	87.0[a]		24.5[b]	

[a] mixed oxides of titanium and zirconium.
[b] mixed oxides of niobium and tantalum.

SUMMARY

A method for the separation and determination of titanium, zirconium, niobium and tantalum is described. Niobium and tantalum are separated with pyrogallol from titanium and zirconium and determined by the N-benzoyl-N-phenyl hydroxylamine method. Pyrogallol is decomposed, and zirconium and titanium are determined by the salicylhydroxamic acid and cupferron methods respectively.

RÉSUMÉ

Une méthode est décrite pour la séparation et le dosage du titane, du zirconium, du niobium et du tantale, les uns en présence des autres. Le pyrogallol permet la séparation du niobium et du tantale d'avec le titane et le zirconium.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Trennung und Bestimmung von Titan, Zirkonium, Niob und Tantal. Niob und Tantal werden von Titan und Zirkonium mit Hilfe von Pyrogallol getrennt. Die weiteren Trennungen erfolgen mit N-benzoyl-N-phenylhydroxylamin, Salicylhydroxamsäure und Kupferron.

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THORIUM DETERMINATIONS WITH 8-HYDROXYQUINALDINE

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The list of organic reagents for the precipitation of thorium was thought "too lengthy" in 1954[1], and since then it has become more so. Some of these reagents have been studied only sparingly. Many yield precipitates that are either variable in composition or unstable at drying temperatures, and for weighing must be ignited to thorium dioxide. In such instances, the favourable gravimetric factor inherent in most organic precipitants is lost, although the reagents may remain useful for effecting separations.

Studies with a thermobalance have proven helpful in comparing and evaluating precipitants for thorium and, in fact, have provided evidence[2] that the possibility of weighing some of the precipitates may have been too hastily rejected. A compound that has good thermal stability[3] is that which thorium forms with 8-hydroxyquinaldine, by the reaction of one mole of thorium with four of the organic reagent[4]. No substantial study of 8-hydroxyquinaldine as an analytical reagent for thorium appears, however, to have been made, although in one context or another this compound has been given considerable attention[5] since the discovery[6] that, unlike the parent compound 8-hydroxyquinoline, it does not precipitate aluminium, a property that is attributed[7,8] to a steric effect of the methyl group in the 2 position in 8-hydroxyquinaldine.

This paper is concerned with the conditions that permit the quantitative precipitation of thorium by 8-hydroxyquinaldine as the 1 : 4 chelate, with gravimetric and bromometric determinations of thorium using this reagent, and with the merits of these.

EXPERIMENTAL

Apparatus

Measurements of pH were made with a Beckman Model G pH meter (Beckman Instruments Inc., South Pasadena, U.S.A.) using a 1190–80 glass electrode for pH values below 10 and a 11–505–75 electrode for values above that, each in association with a saturated calomel reference electrode. Measurements of pH plotted in Fig. 2 were made on the filtrates, after they had cooled to room temperature.

The thermobalance was a Chevenard-type photographically recording instrument (TBP Nr. 27, S.A.D.A.M.E.L., La Chaux de Fonds, Switzerland). The rate of heating was 2.5°/min, and the sensitivity was 0.85 mm/mg.

Reagents

The 8-hydroxyquinaldine was obtained both by synthesis[6] and by the purification (steam distillation, followed by crystallization from 70% ethanol) of a commercial product (Aldrich Chemical Co., Milwaukee, U.S.A.). In each instance, the material was a white crystalline solid, m.p. 71.5–72°.

The thorium nitrate (tetrahydrate) was a highly purified product (Code 103, Lindsay Chemical Co., West Chicago, U.S.A.). Stock solutions of thorium, kept at a pH below 2 with hydrochloric acid, were standardized gravimetrically by precipitation with ammonia and ignition to thorium dioxide[9].

All other chemicals were analyzed grade.

Precipitation of thorium as the 1:4 8-hydroxyquinaldine chelate

We found that the sparse directions available[4] for the precipitation of thorium with 8-hydroxyquinaldine led to a precipitate that, though it contained all the thorium sought (as shown by ignition to thorium dioxide), had only 95%, at most, of the thorium as the 1 : 4 8-hydroxyquinaldine chelate. It appeared that a significant amount of the thorium was being precipitated as hydrous thoria or other hydroxo complexes. A study was therefore made of variables that affect the precipitation of thorium by 8-hydroxyquinaldine, with the objective of developing a simple and reliable procedure for the determination of thorium.

Concentration of reagent

Precipitations were done as set forth in Procedure I, except that the amount of excess 8-hydroxyquinaldine was varied; the precipitates were subsequently treated as in Procedure II, except for the use of low-porosity Selas crucibles instead of fritted-glass ones. The results are in the first two columns of Table I.

TABLE I

EFFECT OF EXCESS 8-HYDROXYQUINALDINE ON THE PRECIPITATION OF THORIUM AS $Th(C_{10}H_8ON)_4$

Concentration of thorium: 0.7 mg/ml. pH of precipitation: 8.1 ± 0.1. Thorium taken was equivalent to 128.6 mg of $Th(C_{10}H_8ON)_4$ and to 39.3 mg of ThO_2.

Excess reagent (%)	*Weight of ppt. (mg)*	*Weight of ThO_2 (mg)*
90	128.5	
65	128.4[a]	39.3
60	128.4	
50	124.2	39.2
35	120.5	39.4
20	108.5	39.0
10	98.4	

[a] This value is an average of 10 determinations (average deviation: 0.2); the other values represent, for the most part, a single determination.

Even though the pH of the solution is appropriate (*vide infra*) for the quantitative precipitation of thorium (from solutions of concentration 0.7 mg Th/ml) the precipitation is not quantitative as the 1 : 4 chelate unless there is a 60% or greater excess of 8-hydroxyquinaldine. The addition of the precipitant "in slight excess"[4] is not a sufficient direction. Ignition to thorium dioxide of the precipitates obtained with an excess of reagent less than 60% showed that the thorium was quantitatively precipitated (Table I), indicating that some of the thorium had precipitated in a form other than the 1 : 4 chelate. With an excess of 60% or greater, however, the precipitation of thorium as the 1 : 4 chelate is not less than 99.8% complete from solutions of concentration 0.7 mg Th/ml. For subsequent precipitations from such solutions, a nearly 70% excess of reagent was used.

A 70% excess is insufficient, however, to precipitate thorium quantitatively as the chelate from solutions with less than about 0.7 mg Th/ml*. From solutions only one-fiftieth as concentrated as this, thorium can nevertheless be precipitated quantitatively if the concentration of 8-hydroxyquinaldine corresponds to 65–70% excess for a solution containing 0.7 mg Th/ml.

Adjustment of pH

The concentration of the aqueous ammonia used to raise the pH to within the desired range, and the way in which the ammonia is added, are important factors in obtaining a precipitate of the pure thorium chelate. If the ammonia is concentrated, the results can be low by as much as 7%, even when the base is added drop by drop, with rapid stirring (Fig. 1, Curve A). In fact, with the ammonia as dilute as 0.5 *M* the results are low (by as much as 1%) if it is added rapidly without stirring. On the other hand, base as concentrated as 1 *M* may be used if added drop by drop, with efficient stirring. Under these conditions, and with a 70% excess of precipitant and the pH adjusted to 8.0–8.5, thorium is quantitatively precipitated solely as the chelate. The average

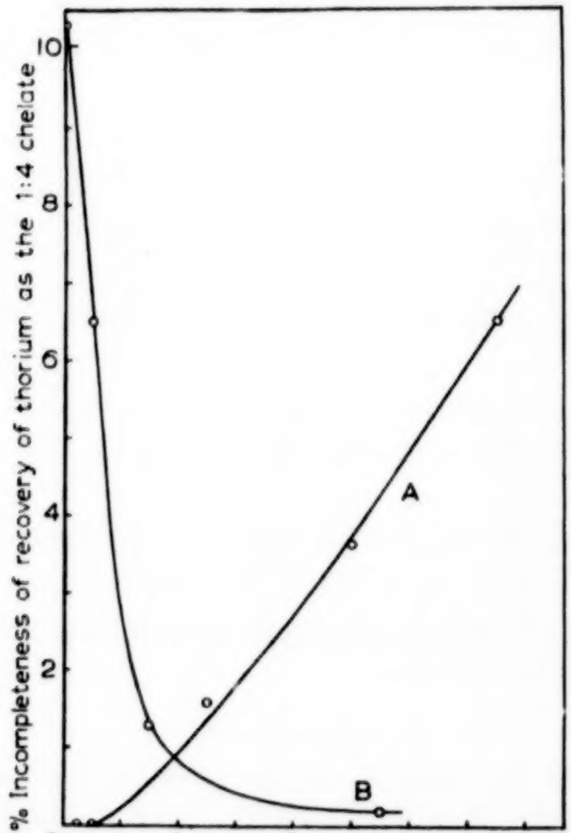

Fig. 1. Effect on recovery of thorium, as $Th(C_{10}H_8ON)_4$, of: (*A*) Molarity of ammonia used to adjust the pH; (*B*) Time of digestion (at 70°C) after pH adjustment by rapid addition of 15 *M* ammonia. In the experiments of Curve A, the ammonia was added drop by drop, with stirring, and the precipitates were digested for one hour at 70°. In the experiments of Curve B, the formation of hydroxo complexes of thorium was encouraged by rapid addition of ammonia, with little regard for stirring. In all experiments, the concentration of thorium in the original solution was 0.7 mg/ml, the pH of precipitation was 8.0–8.5, the excess of precipitant was 70%, and the precipitates were analyzed bromometrically. Each point is the average of at least two determinations; the two lowest points on Curve A summarize 15 determinations.

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* When the pH after precipitation is 8.0–8.5.

of 15 determinations on a solution that contained 33.6 ± 0.1 mg of thorium (concentration 0.7 mg/ml) was 33.7_6 mg, with an average deviation of 0.0_5 mg.

The low results — that is, low as the chelate — induced by adjusting the pH with concentrated ammonia, or even with relatively dilute ammonia added rapidly, are likely due to the precipitation of some of the thorium as hydroxo complexes, occasioned by local excesses of hydroxyl-ion. When local excesses were encouraged by using 5 *M* and 15 *M* ammonia without care in stirring, and when (by eliminating the digestion) the metathesis of any hydroxo complexes to the chelate was hindered, the error rose to over 10%. The error — here calculated as the % thorium not precipitated as the chelate* — was greater the higher the concentration of the added ammonia. Ignition, to thorium dioxide, of precipitates formed under the same conditions showed that the thorium was being precipitated quantitatively: concentration of ammonia, stirring, and digestion affect the nature of the precipitate that is first formed, but not (provided the pH is appropriate) the completeness of precipitation.

If local excesses of hydroxyl-ion initially induce precipitation of some hydroxo complexes when the chelate is the stable form for the precipitate under the conditions existing in the solution, then the hydroxo compounds should in time metathesize to the chelate. The data of Curve B of Fig. 1 show that this occurs. This metathesis was also observed in thermogravimetric experiments. A thermogram for a precipitate digested for only two minutes indicated that the precipitate was not all thorium chelate, whereas the thermogram for a similarly induced precipitate that had been digested for 11 hours was identical with the thermogram of pure chelate.

Provided, then, that the pH be chosen properly (*vide infra*), the thorium will finally be solely (and quantitatively) as the chelate, even though initially some of it precipitates in another form. Under other precipitation conditions (*i.e.*, careful addition of 0.5 or 1 *M* aqueous ammonia) the thorium can be obtained initially (or at least after short digestion) quantitatively as the chelate.

pH control

The data of Fig. 2 show that thorium can be precipitated quantitatively as the chelate in the pH range 6.1 to 11.5, at least with the concentrations of thorium and reagent used. Beginning at a pH of 11.5, precipitation (though complete) is partly as, say, hydrous thoria; by a pH of 13.0, the precipitate is almost entirely hydrous thoria**.

For the experiments summarized in Fig. 2, Procedures I and III were used except that the pH of precipitation was varied over a wide range, with consequent variation in the buffering medium. The solutions were buffered in the acid range by ammonium acetate and acetic acid, and in the alkaline range (to pH 9) by ammonium acetate and ammonia. For pH values above 9, appropriate volumes of 1 *M* and 2 *M* sodium hydroxide were added after the solution had been brought to pH 9 with ammonium acetate and ammonia. Accordingly, the portion of the curve in Fig. 2 for pH values above 9 was not established in properly buffered solutions and the "break-point", shown at pH 11.5, may be a bit in error*.

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* The per cent of the thorium precipitated as the 1 : 4 chelate was determined bromometrically.

** With increasing pH, the concentration of hydroxyl-ion of course increases, but (for a given stoichiometric concentration of 8-hydroxyquinaldine) the concentration of the chelating anion approaches a maximum (corresponding to complete dissociation of the reagent). This leads to the eventual dominance of hydroxyl-ion in controlling the concentration of metal-ion in solution, through the precipitation of hydroxo complexes of thorium ("hydrous thoria") rather than the chelate. The pK_{OH} of 8-hydroxyquinaldine is such that it is largely dissociated by a pH of 11.

The foregoing and related experiments established conditions for the quantitative precipitation of thorium as the 1 : 4 chelate and showed that the precipitate can be dried at 110° to the anhydrous compound, $Th(C_{10}H_8ON)_4$. Other experiments abundantly confirmed earlier observations[4,10] that 8-hydroxyquinaldine can be dibrominated quantitatively. These results led to gravimetric and bromometric procedures for thorium, the details of which follow.

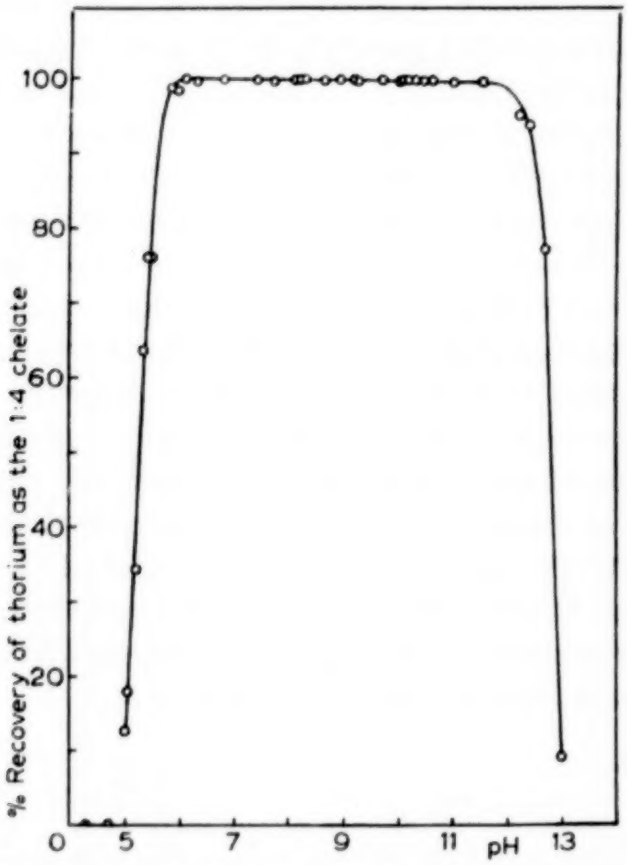

Fig. 2. pH Range for precipitation of thorium as $Th(C_{10}H_8ON)_4$; the concentration of thorium in the original solution was 0.7 mg/ml.

PROCEDURES

1. Precipitation of thorium

Pipet a 50-ml portion of the solution containing thorium at a concentration not higher than 0.7 mg/ml ($3 \cdot 10^{-3}$ *M*) into a beaker. Heat the solution to about 70° and slowly add 8.0 ml of a solution of 8-hydroxyquinaldine (prepared by dissolving 2.0 g of the reagent in 6.3 ml of glacial acetic acid and diluting the solution with water to 100 ml). Then add, slowly with stirring, 2.0 g of ammonium acetate dissolved in 10 ml of hot (70°) water. Adjust the pH to within the range 8–9 (making use of narrow-range pH paper) with 1.0 *M* aqueous ammonia, adding it drop by drop with vigorous stirring. (This should bring the volume to about 90 ml). Finally, allow the precipitate to digest for one hour at about 70°. (Some of the excess 8-hydroxyquinaldine may volatilize during the digestion and condense on the underside of the covering watch glass; this should not be washed down).

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* Since the flat portion of the "pH curve" is broad, a small uncertainty at the "breakpoint" is of little practical significance.

2. *Gravimetric determination of thorium*

After the precipitation and digestion of the precipitate as directed above, allow the solution to cool somewhat and then filter through a medium-porosity fritted-glass crucible and wash the precipitate, using for the transferring and washing about 75 ml of hot 0.15 *M* aqueous ammonia. Dry the precipitate for one hour at 110° ± 5° and weigh as $Th(C_{10}H_8ON)_4$. (The gravimetric factor is 0.2683).

3. *Bromometric determination of thorium*

After the precipitation and digestion of the precipitate as directed in Procedure I, allow the solution to cool somewhat and then filter through No. 40 Whatman paper and wash the precipitate carefully, using for the transferring and washing about 100 ml of hot 0.15 *M* aqueous ammonia. Dissolve the precipitate through the paper, using 50 ml of warm 4 *N* hydrochloric acid, and catch the solution in an iodine flask. Follow the acid with 50 ml of water. To the 8-hydroxyquinaldine solution, now 2 *M* in hydrochloric acid, add 2.0 g of potassium bromide (dissolved in 10 ml of water) and 3 drops of a 0.1% aqueous solution of the sodium salt of methyl red. Titrate, carefully, with standard potassium bromate solution (about 0.02 *M*) until the solution becomes yellow and then add, rapidly, 1.0 to 1.5 ml of the bromate solution. Quickly stopper the flask, and then pour a few ml of a solution of potassium iodide (1.0 g per 10 ml of water) around the lip of the flask. After 5 min, allow the iodide solution to run into the flask and add more, to bring the total added to 10 ml. Immediately titrate the liberated iodine with a standard thiosulfate solution (about 0.1 *M*, standardized against potassium bromate). Calculate the content of 8-hydroxyquinaldine, and hence of thorium, from the titers involved, allowing for the indicator blank.

When less than about 5 mg of thorium is present, the washed precipitate should be dried, while still on the paper, for one hour at 110°, to volatilize coprecipitated 8-hydroxyquinaldine. Then put the precipitate and paper into an iodine flask, treat with 50 ml of warm 4 *N* hydrochloric acid and 50 ml of water, and do the bromination and titration as indicated above.

RESULTS

Gravimetric determination

The very good accuracy and precision of the gravimetric method are shown in Table II. The method is sensitive, too: the precipitation of the thorium chelate can be quantitative from solutions that contained the metal at concentrations as low as 0.012 mg/ml. This value, about $5 \cdot 10^{-5}$ *M*, is the lowest concentration at which experiments were done.

For quantitative precipitation from solutions with less than about 0.7 mg Th/ml an excess of reagent greater than 70% is required, as mentioned earlier. This is provided for in Procedure I, above.

The wash liquid is alkaline to aid in the removal of any coprecipitated 8-hydroxyquinaldine. Even so, when less than about 5 mg of thorium is precipitated (in which event the excess of precipitant is large) the precipitate may retain a significant amount of 8-hydroxyquinaldine. This is of no consequence, for any that remains is volatilized during the drying at 110° (as several experiments proved). Experiments using the thermobalance showed that the thorium chelate can withstand 110°, without detectable volatilization, for at least three hours.

The thermolysis curve found[3] for this thorium chelate was essentially confirmed. The compound has no water of crystallization, and is stable to about 180°.

TABLE II

DETERMINATIONS OF THORIUM AS $Th(C_{10}H_8ON)_4$

Approx. concn. of thorium (mg/l or p.p.m.)	*Thorium taken (mg)*	*Thorium recovered (mg)*[a]	
		Gravimetrically[b]	*Bromometrically*
690	34.51	$34.4_5 \pm 0.0_5$	$34.5_5 \pm 0.0_2$
680	34.1	$34.1_0 \pm 0.0_6$	$34.1_4 \pm 0.0_4$
410	20.4	$20.4_7 \pm 0.0_2$	$20.4_3 \pm 0.0_5$
140	6.81	$6.7_9 \pm 0.0_3$	$6.8_0 \pm 0.0_3$
27	1.36	$1.3_4 \pm 0.0_4$	
12	0.68	$0.6_7 \pm 0.0_3$	$0.6_5 \pm 0.0_2$[c]

[a] Each value is an average of 7–13 determinations; the precision measure is the average deviation.
[b] Weighed as $Th(C_{10}H_8ON)_4$, after drying the precipitate for one hour at 110°.
[c] Precipitates were dried for one hour at 110°, before dissolution in acid, to avoid interference from coprecipitated reagent.

Bromometric determination

Procedure III yields precise determinations of 8-hydroxyquinaldine (and, therefore, of thorium). Some 22 bromometric determinations of thorium (at a concentration of 0.7 mg/ml) gave 33.21 mg with an average deviation of 0.03 mg and a standard deviation of 0.05 mg. The bromometric procedure is fully as accurate as the gravimetric procedure, as results over a wide range of concentrations show (Table II).

We observed, as did BERGES[10], that a very finely divided brown precipitate sometimes forms when the iodide is added. Although the cloudiness due to this precipitate diminishes as the thiosulfate is added, the end-point is obscured with resultant decrease in both precision and accuracy. (Obscure end-points from a similar cause have been encountered[11] in the bromometric determination of 8-hydroxyquinoline.) The amount of the precipitate depends on the amount of excess potassium bromate. In the bromination procedure recommended above, it is entirely avoided by restricting the excess bromate to not more than 1.5 ml.

DISCUSSION

This investigation gave no evidence for any compound of thorium and 8-hydroxyquinaldine (2-methyl-8-hydroxyquinoline) other than that represented by $Th(C_{10}H_8ON)_4$. It is well established, however, that there are two thorium compounds of 8-hydroxyquinoline, of 1 : 4 and 1 : 5 stoichiometry, although there has been disagreement[12] about the temperature ranges over which these are stable. Almost certainly, however, the 1 : 5 compound is not stable above about 80°[13,14]. As consequences of this limitation on the drying temperature, the determination of thorium by weighing this compound not only is lengthy but also is exposed to error from the coprecipitation of the reagent (8-hydroxyquinoline not being appreciably volatile below 85°[14]). In contrast, the 8-hydroxyquinaldine precipitate can be safely dried to the anhydrous 1:4

chelate at 110°, at which temperature 8-hydroxyquinaldine is readily volatilized. The ease with which this chelate may be freed of excess 8-hydroxyquinaldine likewise permits accurate bromometric determinations of thorium by means of this reagent.

The recommended gravimetric and bromometric procedures using 8-hydroxyquinaldine have advantages over commonly used methods for the standardization of thorium solutions. The usefulness of 8-hydroxyquinaldine for determinations of thorium in the presence of other metals is, of course, restricted by the unselective character of this reagent (though its inability to precipitate aluminium gives it a further advantage over 8-hydroxyquinoline).

Under easily achieved conditions, thorium is precipitated by 8-hydroxyquinaldine, quantitatively as the chelate, over fully 5 pH units — a broader pH range for quantitative precipitation than that reported for any other organic precipitant for thorium, insofar as we know.

Under the conditions of our work, the pH of incipient, and of quantitative, precipitation of thorium by 8-hydroxyquinaldine are each substantially higher than the corresponding values found[15], under not greatly different conditions, for the precipitation of thorium by 8-hydroxyquinoline. This is in accord with what has been found[4,7,16] for the precipitation of other metals by these two related reagents. Such comparisons are not really proper, however, unless among other conditions of the experiments the concentrations (both of metal and reagent) are the same, for these influence the pH of precipitation. With all conditions comparable, the difference in the pH of precipitation for the chelates of a given metal with two related reagents should reflect differences in the intrinsic solubility[17] and stability of the chelates, and in the acidity of the reagents. The latter two of these are ordinarily related, in that a given metal commonly forms the more stable chelate with the weaker acid[18]. When this is so, two opposing effects[7,17] bear on the pH of precipitation of the chelate: the more stable of the two chelates does not require as high a concentration of the chelating anion to bring about its precipitation (which argues for a lower pH of precipitation) but, on the other hand, the weaker of the two acids holds protons more firmly and so, to compare with the stronger acid as a provider of the chelating anion, requires a higher pH. A given metal would be expected to form a more stable chelate with 8-hydroxyquinaldine than with 8-hydroxyquinoline, for the former is the weaker acid (both its pK_{NH} and pK_{OH} are higher). In point of fact, however, the 8-hydroxyquinaldine chelates are somewhat less stable, at least in 50% aqueous dioxane[19,20], than the corresponding 8-hydroxyquinoline chelates. (The lesser stability of the 8-hydroxyquinaldine chelates is attributed[19,20] to a steric hindrance to their formation, occasioned by the methyl group in the 2 position in 8-hydroxyquinaldine). Thus, with respect to the precipitation of the chelates of a given metal with these particular reagents, the two factors — chelate stability and reagent anion concentration — should operate, not in opposition but in concert, to favour the precipitation of the 8-hydroxyquinoline chelate at a lower pH than the 8-hydroxyquinaldine chelate.

A reversal of these relative positions for pH of precipitation would be expected only if an 8-hydroxyquinoline chelate had a much higher intrinsic solubility, or was much more prone to supersaturation, than the corresponding 8-hydroxyquinaldine chelate. Neither of these is probable, nor does either appear to be so, for the available experimental data indicate that the chelates of 8-hydroxyquinoline do precipitate at a lower pH than the corresponding chelates of 8-hydroxyquinaldine.

ACKNOWLEDGEMENTS

For financial support of this work and for scholarship awards to one of us (A.C.), we are grateful to the National Research Council of Canada, the International Nickel Company of Canada, Ltd., and the Ontario Research Foundation. We also acknowledge the assistance of Mr. E. E. Wigg with some of the experimental work.

SUMMARY

Conditions under which thorium can be quantitatively precipitated as a 1 : 4 chelate with 8-hydroxyquinaldine have been established. This precipitate can be dried and weighed as the anhydrous compound, $Th(C_{10}H_8ON)_4$, or dissolved in acid and the thorium determined by the dibromination of the released 8-hydroxyquinaldine. Both methods are sensitive, precise and accurate, and have favourable analytical factors; the methods are well suited to the standardization of thorium solutions. 8-Hydroxyquinaldine has distinct advantages over the parent compound, 8-hydroxyquinoline, for the determination of thorium.

RÉSUMÉ

Une étude a été effectuée sur la précipitation du thorium par l'hydroxy-8-quinaldine. Deux méthodes de dosage sont ensuite proposées: 1. Par pesée du précipité $Th(C_{10}H_8ON)_4$; 2. Par titrage iodométrique, après bromuration de l'hydroxy-8-quinaldine en excès. L'hydroxy-8-quinaldine présente des avantages sur l'hydroxy-8-quinoléine.

ZUSAMMENFASSUNG

Zur gravimetrischen Bestimmung von Thorium eignet sich 8-Hydroxychinaldin besser als 8-Hydroxychinolin. Der erhaltene Niederschlag kann als $Th(C_{10}H_8ON)_4$ gewogen oder, nach Auflösen des Niederschlags in Säure, das Thorium bromometrisch bestimmt werden.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES. VIII*

CLÉMENT DUVAL

avec la collaboration technique de

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(Reçu le 2 mars 1960)

Dans cette huitième série, nous présentons une étude thermogravimétrique et spectrophotométrique relative aux douze corps suivants: acétate de baryum, acétate de plomb, nitrate de plomb, nitrate de potassium, chlorure de magnésium, nitrate d'ammonium, citrate d'ammonium, nitrate de cobalt, nitrate d'uranium, téréphtalate de sodium, sulfure de sodium, palmitate de potassium.

Toutes ces substances ont été chauffées sur la thermobalance à enregistrement photographique, avec échauffement linéaire de 300° par heure et avec des poids de substance de l'ordre de 200 mg. Les spectres infrarouges ont été realisés sur poudre, avec vaseline comme agglomérant, entre 6 et 15 μ, sur le spectromètre Perkin-Elmer 12C, avec optique de chlorure de sodium.

Acétate de baryum

Le produit commercial utilisé, pris dans un flacon déjà ouvert, correspond au monohydrate; il n'est pas hygroscopique et on peut le peser tel quel. Si l'on voulait prendre le sel anhydre, il conviendrait de porter cet hydrate en thermostat vers 105°. La déshydratation s'effectue normalement entre 72 et 96°; le sel anhydre reste à peu près stable jusqu'à 240°; il perd lentement du poids jusqu'à 480° et le départ d'acétone s'effectue jusqu'à 542°. Le résidu, à poids constant, est constitué par le carbonate de baryum suivant une réaction très classique qui semble remonter à Chenevix (Fig. 1).

Le spectre infrarouge nous permet de mesurer les fréquences suivantes: 931 (F), 1021 (F), 1053 (aF), 1347 (f), 1419 (F), 1542 (TF) cm^{-1}.

Acétate de plomb

Ce sel signalé avec 3 molécules d'eau pour les usages analytiques, nous en a accusé un peu moins si l'on tient compte du poids du résidu (environ 2.3 H_2O). De toute façon, on ne peut guère l'utiliser pour faire une pesée directe car il se déshydrate dès la température ordinaire (Fig. 2) et la perte d'eau est déjà sensible à 44°. Sa déshydratation se poursuit jusque vers 100° mais le produit anhydre ne fournit pas de palier horizontal. Sa dissociation est achevée à 448°; au-delà nous réalisons le palier sensiblement horizontal de l'oxyde de plomb PbO.

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* Pour le septième mémoire de cette série, voir *Anal. Chim. Acta*, 20 (1959) 263.

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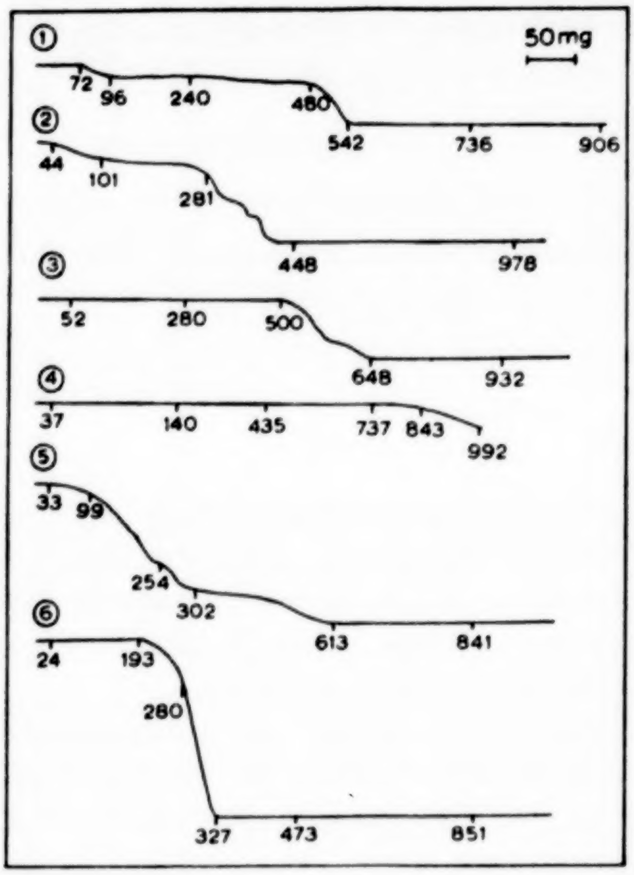
Le spectre infrarouge nous a permis d'enregistrer et de mesurer les fréquences suivantes: 933.5 (aF), 1020 (aF), 1051 (f), 1337 (aF), 1405 (F), 1550 (TF) cm^{-1}.



Figs. 1–6.

Nitrate de plomb

Le nitrate de plomb cristallise anhydre. Sa courbe de thermolyse indique qu'il est stable jusqu'à 280°, puis la dissociation s'amorce lentement jusqu'à 500°; elle s'accélère ensuite et à 648°, on obtient le palier horizontal de l'oxyde PbO (Fig. 3). Pour faire une liqueur titrée il est donc possible de peser le nitrate de plomb tel quel, en le prélevant du flacon.

Le spectre infrarouge, réalisé sur poudre, est tout à fait en accord avec celui de MILLER ET WILKINS[1] et présente dans la région étudiée les quatre bandes suivantes: 725.5 (F), 806.5 (aF), 838 (aF), 1369 (F), plus un épaulement au voisinage de 1306 cm^{-1}.

Nitrate de potassium

Ce sel est anhydre et stable depuis la température ordinaire jusqu'à 737° au moins. Toutefois, un examen minutieux de la courbe (Fig. 4) semble indiquer une légère dissociation portant sur 1/200 du poids soumis à l'expérience dès 140°. La décomposition ne devient appréciable que vers 843°. Rappelons, en accord avec divers auteurs, qu'il se forme du nitrite de potassium et des vapeurs nitreuses et que le passage par le point de fusion situé vers 339° ne se signale par aucune dissociation nette.

Le spectre infrarouge, déjà mesuré par de nombreux auteurs, en particulier par MILLER ET WILKINS[1], nous a présenté, dans la région précitée, les deux bandes fortes fondamentales à 825 et 1394 cm^{-1}.

Chlorure de magnésium

Ce corps déliquescent, soumis à une recristallisation, contient 5.6 molécules d'eau qu'il commence à perdre dès la température ordinaire. Il est donc impossible de confectionner une liqueur titrée par pesée directe et, de plus, la déshydratation ne conduit pas à un palier du sel anhydre (Fig. 5) parce qu'avec nos conditions opératoires, la vapeur d'eau libérée produit la décomposition et on arrive au palier de l'oxyde de magnésium MgO à partir de 613°.

Le chlorure de magnésium hydraté ne donne pas et ne doit pas donner de spectre infrarouge dans le région du chlorure de sodium, à l'exclusion de la bande caractéristique de l'eau.

Nitrate d'ammonium

Ce sel, vendu anhydre, a été séché préalablement dans le dessiccateur avec anhydride phosphorique car on sait que l'eau intervient dans la vitesse et la température de décomposition. Lorsque le flacon a été ouvert plusieurs fois, il est bon de porter le sel à une température inférieure à 193° car il se montre hygroscopique. C'est à cette dernière température que la sublimation et la décomposition en vapeur d'eau et oxyde azoteux commencent à se faire sentir et cette dernière s'accélère brusquement vers 280° en accord avec d'autres auteurs, pour s'achever, d'une manière nette, vers 327° (Fig. 6). Le palier qui suit est relatif au poids du creuset vide.

On sait que ce sel peut exister sous cinq modifications cristallines dont les spectres infrarouges sont différents. Le produit pur pour analyses, que nous avons utilisé, présentait deux bandes fortes relatives à NO_3 pour 837 et 1370 cm^{-1} et une bande relative à NH_4 pour 1405 cm^{-1}.

Citrate d'ammonium

Le citrate diammonique que nous avons utilisé $(NH_4)_2HC_6H_5O_7$ était anhydre et bien sec. Il s'est montré stable jusqu'à 161°; après quoi, la décomposition et la combustion se produisent sans accident; le creuset est vide vers 630°; les dernières traces de carbone sont longues à brûler (Fig. 7).

Le spectre d'absorption infrarouge accuse les bandes suivantes, bien marquées et assez fortes: 833, 892, 922, 1090, 1110, 1210, 1240, 1297, 1365 et 1435 cm^{-1}.

Nitrate de cobalt(II)

Ce sel est très déliquescent et contient ordinairement plus de 6 molécules d'eau. Il est à peu près impossible d'en faire une liqueur titrée par pesée directe car il se déshydrate d'une façon continue et perceptible dès 34°. La dissociation ne se distingue pas de la déshydratation avec notre vitesse de chauffe et se ralentit beaucoup aux approches de 290° (Fig. 8). Un palier légèrement oblique s'étend jusque vers 700°, température au-dessus de laquelle, on obtient l'oxyde Co_3O_4.

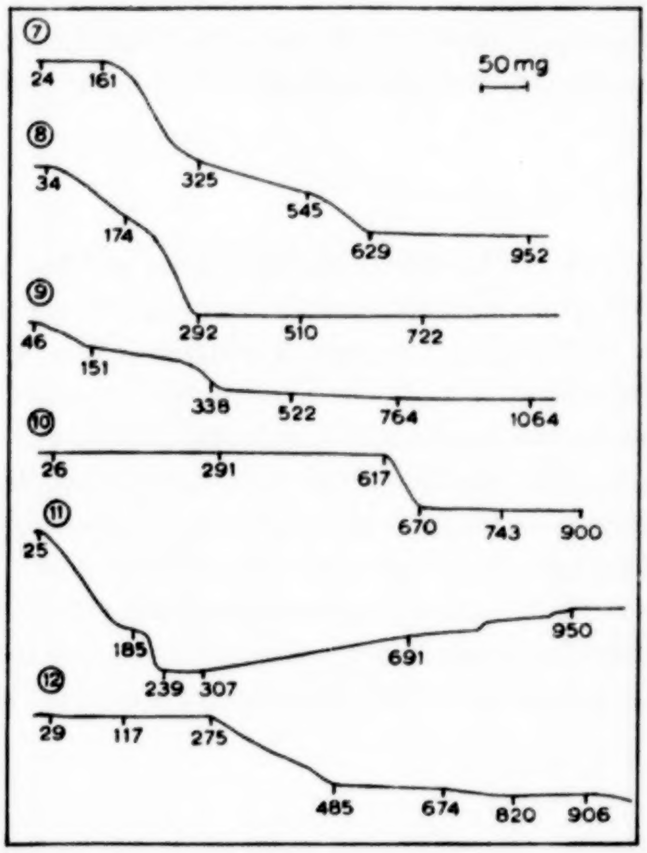
Le spectre infrarouge, réalisé sur un produit beaucoup plus sec, nous a donné les bandes: 837.2 (F), 1380 (F) cm^{-1}.

Nitrate d'uranyle

Le nitrate d'uranyle est un sel hexahydraté bien sec, mais il se montre à peine plus stable que le nitrate de cobalt(II). En effet, il commence à se déshydrater dès 46°;

on ne peut pas faire la distinction entre la perte d'eau et la décomposition (Fig. 9). Toutefois, vers 350°, la vitesse diminue quand on approche du résidu UO_3, lequel perd à son tour de l'oxygène et dès 760°, on aboutit à l'oxyde U_3O_8. Il est permis de faire une liqueur titrée avec le sel extrait d'un flacon neuf.

A côté des bandes fortes de 943 et 1034 cm^{-1} relatives à UO_3, nous avons enregistré dans le spectre infrarouge, deux autres bandes fortes, l'une à 839, l'autre à 1350 cm^{-1}.



Figs. 7–12.

Téréphtalate de sodium

Ce sel est stable au moins jusqu'à 300° et se montre anhydre. La perte de poids qu'il éprouve ensuite jusqu'à 617° est vraiment minime mais la décomposition se produit brusquement entre 617 et 670°. Le carbone résiduel brûle extrêmement lentement et vers 840° le creuset est vide (Fig. 10).

Le spectre infrarouge permet d'enregistrer les maxima suivants: 746 (F), 760 (f), 826 (F), 895 (f), 1023 (f), 1397 (TF), 1566 (TF) cm^{-1}.

Sulfure de sodium

Le sulfure de sodium incolore utilisé, contient à peu près 9 molécules d'eau lorsqu'on le sort du flacon pour la première fois, mais il est très hygroscopique. Il est difficile d'en faire directement une liqueur titrée car sa déshydratation commence vers 30°. La courbe tracée (Fig. 11) indique que le produit anhydre donne un palier à peu près horizontal entre 240 et 307°; après quoi, la courbe remonte à peu près linéairement et vers 950°, on arrive au sulfite de sodium qui n'est pas rigoureusement pur. Ce sel ne donne pas de spectre infrarouge dans la région du chlorure de sodium.

Palmitate de potassium

Le palmitate de potassium, légèrement humide tel que nous l'avons utilisé, devient

sec et montre un poids constant de 40 à 275°. A cette température la décomposition s'amorce et s'effectue progressivement jusqu'à 485°; alors le carbone brûle lentement et le creuset est vide à 820° (Fig. 12). Il faudra donc sécher ce corps, d'aspect savonneux, avant sa pesée.

Le spectre infrarouge permet d'enregistrer les bandes suivantes: 913 (aF), 1010 (f), 1095 (f), 1379 (aF) et 1437 (F) cm^{-1}.

RÉSUMÉ

Nous avons tracé la courbe de thermolyse et donné le spectre d'absorption infrarouge sur solide, de douze substances pouvant servir comme étalons. L'acétate de plomb, le chlorure de magnésium, le nitrate de cobalt(II) et le sulfure de sodium ne peuvent être pesés directement pour confectionner une liqueur titrée.

SUMMARY

Description of the thermolysis curves of 12 substances; determination of their i.r. absorption spectra in order to examine whether or not they are suitable as standards. It was found that lead acetate, magnesium chloride, cobalt(II) nitrate, and sodium sulphide cannot be weighed directly for the preparation of a standard solution.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung von Standardsubstanzen auf deren Eignung als solche auf Grund von IR Spektren und thermolytischem Verhalten. Bleiacetat, Magnesiumchlorid, Kobaltnitrat und Natriumsulfid können nicht direkt gewogen werden zur Herstellung von Normallösungen.

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ACID ALIZARIN BLACK SN METALLOCHROMIC INDICATOR FOR CALCIUM

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The development which made ethylenediaminetetraacetic acid (EDTA) a reagent of practical significance was undoubtedly the evolution by SCHWARZENBACH, BIEDERMANN AND BANGERTER of the complexometric water-hardness determination based on the use of Eriochrome Black T and Murexide as visual indicators[1]. However, many newer indicators have been proposed for this determination and a recent examination has shown that with these, results may vary markedly[2]. Unquestionably, in dilute calcium solution, one of the most clear-cut end-points is obtained with the tris-hydroxy bis-azo dyestuff Acid Alizarin Black SN (C. I. Mordant Black 25). One of the peculiar features of this indicator, however, is that it gives a much sharper

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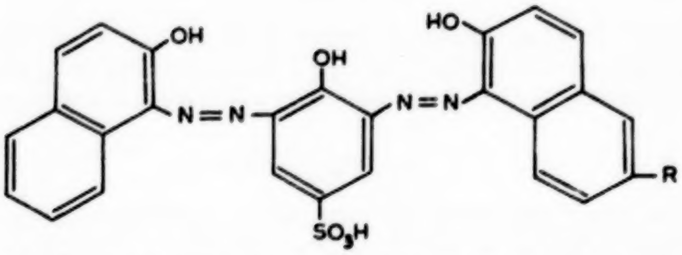
end-point in dilute (0.01 *M*) calcium solution than it does in strong (0.1 *M*) solution. This paper reports an examination of this phenomenon and discusses the suitability of Acid Alizarin Black SN and the closely related dyestuff Acid Alizarin Black SE as metallochromic indicators for cations other than calcium.

Metallochromic properties of Acid Alizarin Black SN and SE



R = —SO$_3$H: Acid Alizarin Black SN (C.I. Mordant Black 25),
R = —H: Acid Alizarin Black SE (C.I. Mordant Black 10).

In common with all other metallochromic reagents of the hydroxy-azo or hydroxy aminomethyl (dicarboxymethyl) variety, both molecules function as acid–base indicators. Thus AABSN is red-coloured below pH 5.4, turquoise blue between pH 6.5–12.4 and gradually assumes a purple shade at pH > 12.8. AABSE behaves similarly.

Both dyestuffs were tested as metallochromic reagents and for this purpose were used as a 0.1% aqueous solution (AABSN) or as a 2% dispersion on pulverised sodium chloride (AABSE). Particular attention was paid to reactions with the alkaline earths and towards metals of the alkali-sulphide group. In all cases the colour changes produced on chelation of the dyestuff with a metal ion were found to be hypsochromic.

AABSN gave a red-purple to blue end-point in the titration of 0.02 *M barium* with EDTA in an ammonium hydroxide solution at pH 11.5; the colour change was gradual over a few drops of titrant. The use of a diethylamine buffer at pH 12.5 did not improve matters. With *calcium* the same indicator gave a very sharp (1 drop) red to turquoise end-point between pH 11.5–12.5 using ammonia, diethylamine or sodium hydroxide buffers. *Strontium* behaved similarly, giving sharp red to turquoise end-points in the same media; *magnesium* afforded only unsatisfactory vague end-points from red-purple to blue over the range pH 8.5–10 in all media examined. With *cadmium*, AABSN yielded a sharp red to blue end-point at pH 8.5 in a borax buffer; an indistinct purple to turquoise end-point was obtained in ammonia at pH 11.5 and none whatsoever in ammonia–ammonium chloride at pH 10. Optimum conditions for *manganese* were obtained with a very sharp purple to turquoise end-point at pH 10 in ammonia–ammonium chloride buffer. Less well defined end-points were obtained at pH 8.5 and 11.5. *Nickel* gave a sharp purple to turquoise-blue end-point in hot solution at pH 11.5 (ammonia) and *zinc* behaved similarly. Of the other ions examined only *thorium* deserves special mention. It was observed to give a very sharp crimson to orange end-point at pH 4 in a sodium acetate–acetic acid buffer.

AABSE was found, rather surprisingly, to be very much inferior as an indicator for all the above ions (only with calcium was a reasonable red to blue end-point obtained, but even this was inferior to the AABSN end-point). In addition, AABSE was observed to give a purple to blue end-point with copper(II) over the entire pH range 4–11.5, but the response was rather too sluggish for indicator purposes.

Although the two molecules differ only in that AABSN contains an extra sulphonic acid group, which is not involved directly in the chelating action, there is a marked difference in their metallochromic properties; it is perhaps most noticeable with thorium, copper and calcium. Since the reaction of these indicators with calcium was judged to be of most analytical significance, further examination was confined to the calcium chelates.

Reaction of AABSN with calcium

It was observed that whereas AABSN gave a sharp, but poorly defined purple to turquoise end-point in the titration of calcium at the 0.1 *M* dilution level a much more clear-cut end-point was obtained in $\leqslant$ 0.02 *M* solutions. In the latter instance the colour of the solution was purple over 90% of the titration, but near the end, the colour changed to red and passed sharply through to turquoise at the equivalence point. This performance suggested the possibility of the calcium and indicator ions reacting to form more than one complex. Accordingly, it was decided to investigate the spectrophotometry of chelate formation to obtain evidence in support of this theory.

Since the sample of dyestuff available to us was of commercial origin, it was first of all assayed and found to be only 88% pure. A pure product was obtained from the commercial material by extracting its aqueous solution with benzene, ether and finally chloroform. The aqueous solution was evaporated to dryness, dissolved in methanol and saturated with gaseous hydrochloric acid. The solution was then filtered and evaporated to crystallisation point. The dark red crystals thus obtained were removed and dried under vacuum over caustic soda. It should perhaps be stressed at this point that the commercially available material is entirely adequate for normal indicator purposes and the above purification procedure was only necessary to obtain a sample for quantitative studies on the pure dye itself.

The spectrophotometric examination was made with $5 \cdot 10^{-4}$ *M* aqueous calcium and indicator solutions in a diethylamine buffer system. Fig. 1 shows the absorption spectra of the free dyestuff at pH 12.5 (A), the dyestuff in the presence of a $\frac{1}{2}$ molar ratio of calcium ions (B), and the dyestuff in the presence of a large excess of calcium

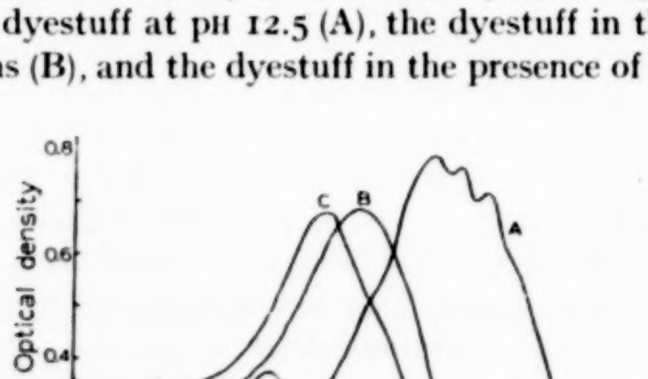


Fig. 1. Acid Alizarin Black SN. A, free indicator, pH 12.5; B, indicator + excess Ca^{+2}; C, indicator + 1/2 mole Ca^{+2}.

ions (C). The three spectra therefore represent the forms of the chromogenic species beyond the end-point immediately before it and as it would be during the bulk of a titration in dilute solution. This experiment reveals the presence of a bright red complex between the indicator and calcium, λ_{max} 548 mμ, when low concentrations of calcium are present and of a purple complex, λ_{max} 573 mμ, when there are preponderant amounts of calcium. The main absorption band of the metal-free indicator at this pH is broader and shows triplet peaks in order of decreasing intensity at 632, 652 and 673 mμ. In addition the free dyestuff shows a distinct absorption band of low intensity at 507 mμ.

Thus the existence of more than one indicator complex between calcium and the dyestuff is suggested.

Fig. 2 shows the spectra obtained in a repeat experiment with AABSE in place of AABSN. In this instance the purity of the commercial material was found to be *ca.* 83%, but since this dyestuff was much less soluble in water it was not found entirely practicable to take it through the same purification procedure as AABSN. Consequently we contented ourselves by removing the bulk of impurities, which were inorganic in nature, by recrystallising from methanol. Whilst this may not have removed traces of organic impurities, the expected close similarity in overall structure of the absorption spectrum of the metal-free dyestuff to that of AABSN substantiates the purity of the sample. In this instance it will be seen that in the presence of a small amount of calcium a complex is formed with $\lambda_{max} = 550$ mμ. The presence of a large excess of calcium yields an absorption band of much higher intensity (*cf.* AABSN) with only a 10 mμ increase in the wavelength of maximum absorption. The shape of the two spectra are very similar. The metal-free dyestuff shows a main absorption band, $\lambda_{max} = 636$ mμ, with a sharp band of low intensity at 509 mμ. This experiment clearly shows that the separation between the various absorbing species with AABSE is somewhat less and that whilst there is a suggestion that two complexes may exist there is a much smaller separation between the two bands and also a considerable difference in extinction.

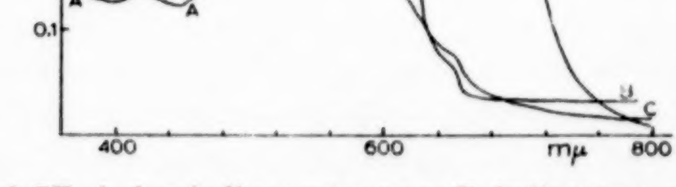


Fig. 2. Acid Alizarin Black SE. A, free indicator pH, 12.5; B, indicator + excess Ca^{+2}; C, indicator + mole ratio Ca^{+2}.

The structure of the chelate formed between calcium and AABSN were then determined by a procedure of continuous variations. For the red complex, measurements were made at 545 mμ, *i.e.* following the formation of the red complex and at 630 mμ following the disappearance of the blue dyestuff. The corrected plot of the former is shown in Fig. 3 (A). Both experiments give clear-cut evidence of the existence of a fairly well defined complex in what the AABSN–calcium ratio is 2 : 1.

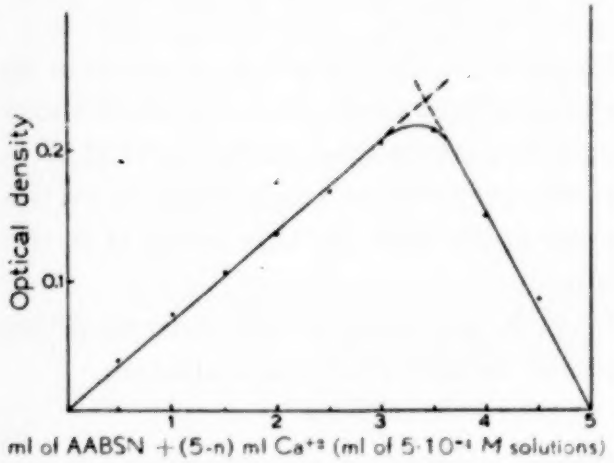


Fig. 3. (A) Acid Alizarin Black SN, 2 : 1 chelate, corrected continuous variations plot, $\lambda = 545$ mμ.

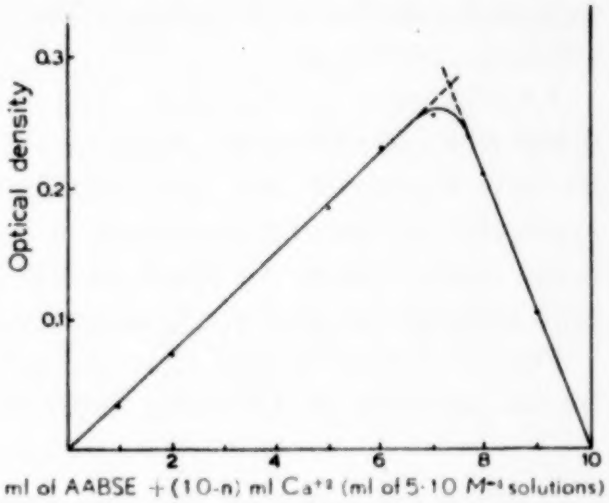


Fig. 3. (B) Acid Alizarin Black SE, calcium complex, corrected continuous variations plot, $\lambda = 560$ mμ.

Similar experiments conducted at 570 mμ suggested evidence of a rather weak complex in which there is AABSN–calcium ratio of 1 : 1. Best results were obtained in this instance by studying the variations procedure between calcium and a solution containing the 2 : 1 AABSN–calcium formulation.

With AABSE evidence could only be obtained of a 2 : 1 chelate of Fig. 3 (B). Variation procedures were made at 560 mμ and at 635 mμ again following the formation of the purple complex and the consumption of the metal-free dyestuff. Both experiments give evidence of a strong well defined 2 : 1 reagent–calcium complex.

DISCUSSION

As a result of the above examination it is evident that AABSN forms a stable 2 : 1 chelate with calcium ion in dilute solution. When large amounts of calcium are present a 1 : 1 chelate is formed, but this is a considerably weaker complex. It is of interest to note that the extinction value of the 2 : 1 and 1 : 1 chelates are almost equal. The maximum absorption of the red-form (end-point species) is separated from that of the metal free dyestuff at the same pH by *ca.* 100 mμ. The wavelength separation for the 1 : 1 chelate and the free dye is *ca* 80 mμ and there is considerably more overlap of the absorption spectra of the two forms (*cf.* Fig. 1). Normally in a titration only a few drops of indicator are added. Consequently in using 0.1 M Ca^{+2} solutions, the chance of the 2 : 1 indicator–calcium chelate appearing in solution is very slight. Thus though the end-point is sharp (80-mμ shift) there is not a great colour contrast. In dilute solution ($\leqslant 0.02$ M Ca^{+2}) there is a distinct possibility of the 2 : 1 chelate being formed before the titration has proceeded to the end-point. Consequently a much more distinct end-point is obtained.

With AABSE it is debatable whether the 10-mμ shift observed in λ_{max} for the metal-indicator complex is due to the existence of more than one complex and the marked increase in the extinction value tends to suggest that there may in fact only be one. We could find no definite evidence of the existence of anything other than a 2 : 1 indicator–calcium chelate in this instance from spectrophotometric studies of continuous variation and conclude that with AABSE the poorer end-point is entirely due to the inferior separation (86 mμ between the λ_{max} values for the metal-free indicator and the 2 : 1 chelate). The overlap between the spectra is also very considerable, *cf.* Fig. 2.

AABSN gives a very sharp well defined end-point in the titration of calcium in dilute solution and in our experience it is the sharpest and most clear cut of all those we have examined. We have also found[2] that it is particularly useful in that it is applicable for the determination of calcium in the presence of magnesium over the range where Calcon (CI Mordant Black 17) is not applicable. In this range it is the only indicator to give 100% recovery of calcium.

Finally it may be said that the indicator AABSN has considerable potentialities for the titration of strontium, thorium, manganese, nickel, zinc and cadmium.

EXPERIMENTAL

Reagents for titration of calcium

0.01 M EDTA: Prepared from disodium ethylenediaminetetraacetic acid, dihydrate dissolved in glass-distilled or de-ionised water and standardised against pure magnesium metal using Solochrome Black 6 B as indicator[3] at pH 10; *0.01 M CaCl$_2$*: Prepared from oven-dried AR grade calcium carbonate dissolved in a slight excess of 0.1 *N* HCl and diluted to volume; *Diethylamine; Acid Alizarin Black SN;* 0.1% aqueous solution.

Procedure

25.00 ml of 0.01 *M* calcium chloride were pipetted into a 250-ml conical flask and the solution was diluted to 50–70 ml with distilled water. 2 ml of diethylamine buffer were added and 5–6 drops of indicator solution. The solution was then titrated rapidly with 0.01 *M* EDTA till the warning red shade of the 2 : 1 indicator–calcium chelate appeared a few drops from the end-point. The titration was then completed dropwise till the red colour changed sharply to turquoise-blue.

ACKNOWLEDGEMENT

We wish to thank the Clayton Aniline Company for the award of a research studentship to one of us (R.A.C.) and we are indebted to the same organisation for the provision of the original sample of both dyes used in the examination.

SUMMARY

The metallochromic properties of the closely related tris-hydroxy bis-azo dyestuffs Acid Alizarin Black-SN and -SE are examined. The former is shown to be a particularly excellent complexometric indicator for calcium in dilute solution and is also recommended for strontium, manganese, nickel, zinc, cadmium and thorium. Both indicators are shown to form 2: 1 indicator–calcium chelates, on the basis of spectrophotometric evidence, and the unusual behaviour of the former indicator in strong calcium solutions is explained.

RÉSUMÉ

Le noir acide d'alizarine SN est proposé comme indicateur pour le titrage complexométrique du calcium, au moyen de l'éthylènediaminotétracétate disodique. Il peut être recommandé également pour le strontium, le manganèse, le nickel, le zinc, le cadmium et le thorium.

ZUSAMMENFASSUNG

Als Indikatoren bei der komplexometrischen Titration von Calcium, Strontium, Mangan, Nickel, Zink, Cadmium und Thorium mit Äthylendiaminotetraessigsäure (Natriumsalz) eignen sich die Säuren von Alizarinschwarz SN und SE.

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RADIOCHEMICAL SEPARATION OF ^{95}Zr AND ^{95}Nb WITH TRI-*n*-BUTYL PHOSPHINE OXIDE

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INTRODUCTION

Tri-*n*-octyl phosphine oxide is an excellent extractant for zirconium, the extraction of which from acidic solutions has been studied[1]. In the course of a study on the extraction of zirconium with organophosphorus compounds, it was observed that the extraction behaviors of ^{95}Zr and ^{95}Nb with tri-*n*-butyl phosphine oxide (TBPO) are quite different so that their mutual separation should be possible. Several methods including anion-exchange resins[2–5], cation-exchange resins[6,7] and TTA extraction[8], have been used for the separation of ^{95}Zr and its daughter ^{95}Nb. Extraction by tri-*n*-butyl phosphine oxide from nitric acid solution provides a rapid and efficient separation method for these isotopes, and the present article describes the details of the procedure.

EXPERIMENTAL

Chemicals

Tracer ^{95}Zr and its daughter ^{95}Nb: The tracer ^{95}Zr was supplied by Oak Ridge National Laboratory in the form of oxalate. The ^{95}Zr oxalate was converted to nitrate by repeated boiling and evaporation with concentrated nitric acid, and finally dissolved in 6 *N* nitric acid. Tri-*n*-butyl phosphine oxide: The tri-*n*-butyl phosphine oxide was obtained from Tama Chemicals, Tokyo, Japan, and was dissolved in carbon tetrachloride at concentrations of 0.001, 0.002, 0.005, 0.01, 0.02, 0.05 and 0.1 *M*. Other chemicals such as nitric acid and carbon tetrachloride were of reagent grade, and the carbon tetrachloride was purified by the distillation before use.

Preliminary test

Nitric acid (2 *N*) solutions containing ^{95}Zr and ^{95}Nb in radio-chemical equilibrium were shaken with equal volumes of 0.01 *M* TBPO, and the organic and the aqueous phases were then separated. The organic phase was repeatedly washed with 2 *N* HNO_3 pre-equilibrated with 0.01 *M* TBPO, and the aqueous phase was washed with 0.01 *M* TBPO pre-equilibrated with 2 *N* HNO_3. In the organic phase, the species with the *Kd* value of ∼ 100 was collected, whereas the species with the *Kd* value of ∼ 0.1 was found in the aqueous phase. The measurement of both absorption curves and half lives identified these species as ^{95}Zr in the organic phase and ^{95}Nb in the aqueous phase.

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RESULTS

Distribution coefficients of ^{95}Zr and ^{95}Nb

The species obtained by the preliminary test were identified as pure ^{95}Zr and ^{95}Nb, and the distribution coefficients of these species were determined over the nitric acid concentration range of 1–13 *N*. The results are shown in the Fig. 1. The effect of solvent concentrations on the distribution coefficients was then studied at a fixed nitric acid concentration of 2 *N*; the results are shown in the Fig. 2.

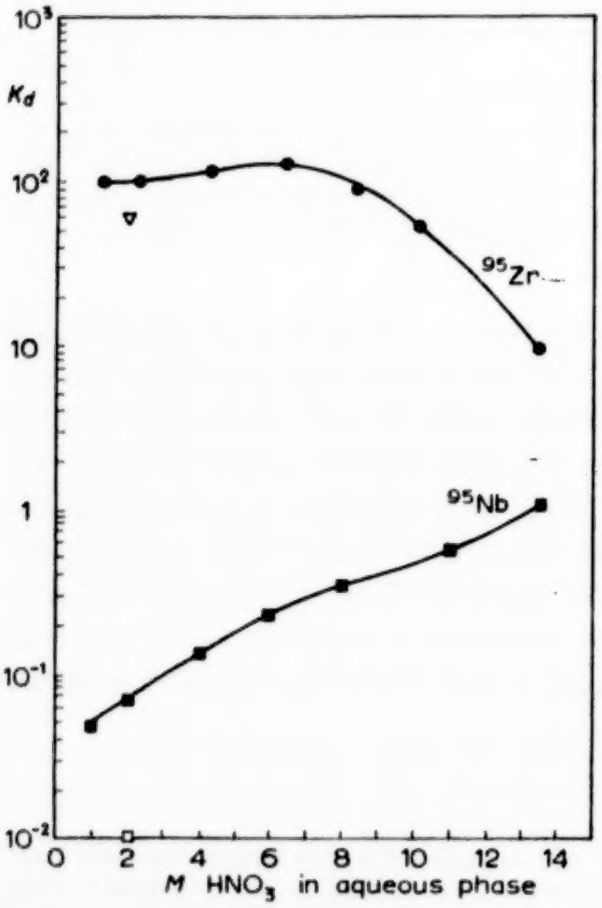

Fig. 1. Distribution coefficients of ^{95}Zr and ^{95}Nb with 0.01 *M* TBPO. ▽ and ☐ indicates the *Kd* values with 0.005 *M* TBPO.

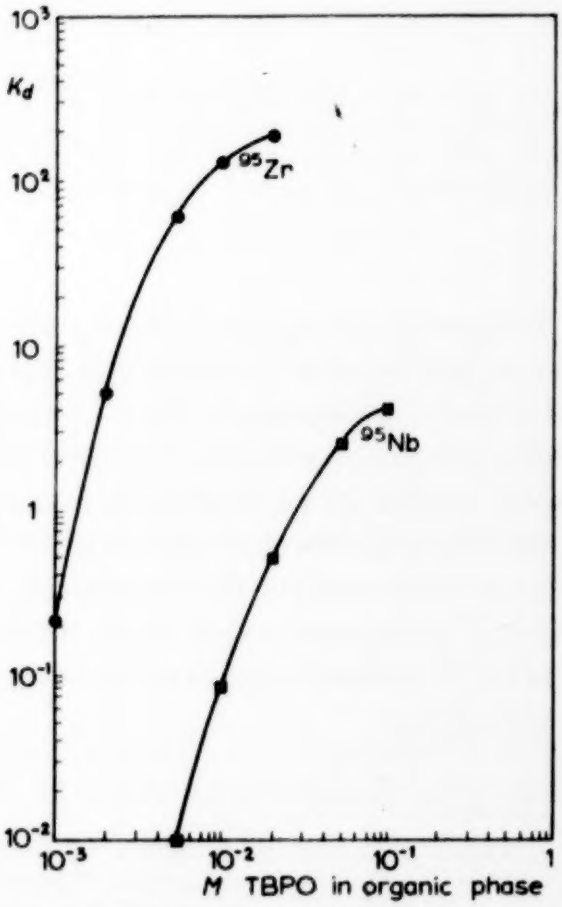

Fig. 2. Distribution coefficients of ^{95}Zr and ^{95}Nb with various TBPO concentrations and a 2 *M* HNO_3 aqueous phase.

Proposed procedure for the separation

If ^{95}Zr and ^{95}Nb in radiochemical equilibrium are separated completely, the activity ratio should be about 1 : 2 which gives a measure of the optimum TBPO concentration; on extraction with 0.005 *M* TBPO, the activity ratio of two phases was determined to be 1 : 2. As regards the nitric acid concentration, the lower the concentration, the better the separation, but the choice of nitric acid concentration is restricted because of the possible hydrolysis of the species in aqueous phase below 2 N HNO_3; a 2 N nitric acid solution was therefore selected.

Equal volumes of the 2 N nitric acid stock solution of ^{95}Zr and ^{95}Nb and of 0.005 M TBPO in carbon tetrachloride were shaken, and the aqueous and the organic phases were separated. ^{95}Zr was extracted into the organic phase, whereas ^{95}Nb remained in the aqueous phase. The organic phase was washed with an equal volume of 2 N nitric acid pre-equilibrated with 0.005 M TBPO, and then diluted with an equal volume of carbon tetrachloride. The back-extraction of ^{95}Zr was made with concentrated nitric acid; the repetition of the back-extraction with concentrated nitric acid gave a 95% yield of ^{95}Zr. The back-extract was washed with carbon tetrachloride to remove the remaining TBPO. The aqueous phase which contained ^{95}Nb was washed with 0.005 M

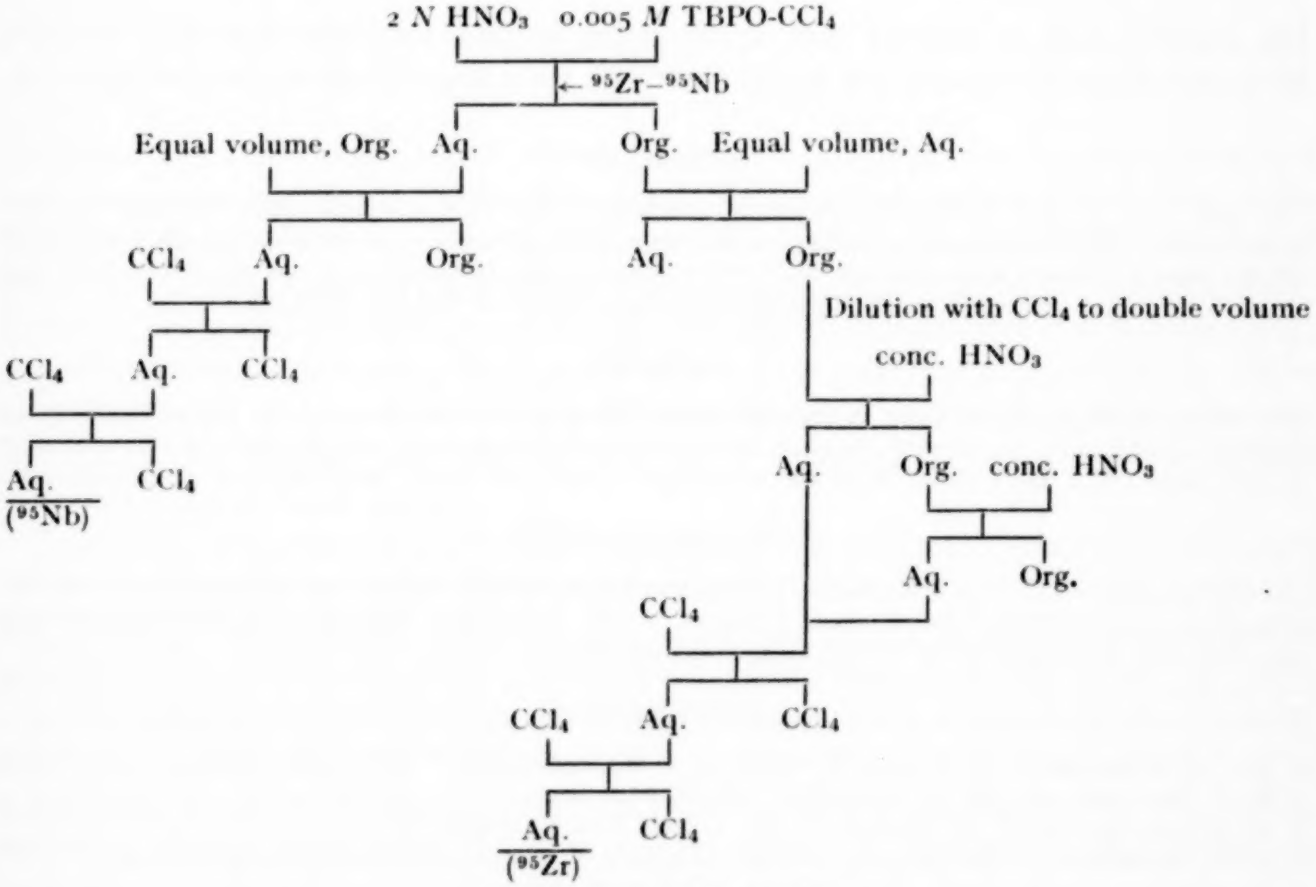
2 N HNO₃
0.005 M TBPO-CCl₄
← ⁹⁵Zr–⁹⁵Nb
Equal volume, Org.
Aq.
Org.
Equal volume, Aq.
CCl₄
Aq.
Org.
Aq.
Org.
Dilution with CCl₄ to double volume
conc. HNO₃
CCl₄
Aq.
CCl₄
CCl₄
Aq.
Org.
conc. HNO₃
Aq.
CCl₄
(⁹⁵Nb)
Aq.
Org.
CCl₄
CCl₄
Aq.
CCl₄
CCl₄
Aq.
CCl₄
(⁹⁵Zr)

Fig. 3. Separation scheme.

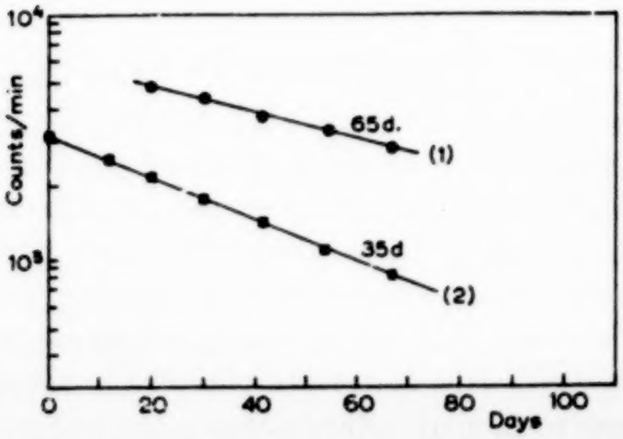

Fig. 4. Half-lives of the separation products. (1) Species collected in the organic phase (^{95}Zr). (2) Species collected in the aqueous phase (^{95}Nb).

TBPO pre-equilibrated with 2 N HNO_3 and then with carbon tetrachloride to remove any remaining TBPO. The entire separation scheme is illustrated in the Fig. 3.

The *Kd* values of ^{95}Zr and ^{95}Nb thus separated were compared to these listed[1], and good agreement was observed. The absorption curves and half lives confirmed that the ^{95}Zr and ^{95}Nb obtained were in a pure form. The half lives of the separated species are shown in the Fig. 4.

The scrubbing solution must be pre-equilibrated with the solvent because of the appreciable solubility of TBPO in water. The extraction of ^{95}Zr and ^{95}Nb from hydrochloric acid solution was examined, but the distribution coefficients were too close, and the separation was not possible.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to Drs. KENJIRO KIMURA, TAKASHI MUKAIBO, KEIICHI OSHIMA and KEIJI NAITO for their suggestions and encouragement.

SUMMARY

^{95}Zr and ^{95}Nb behave differently on extraction from nitric acid solutions with tri-*n*-butyl phosphine oxide (TBPO). These isotopes can be separated efficiently by extraction with 0.005 M TBPO from 2 N nitric acid solution. ^{95}Zr was extracted into the organic phase and ^{95}Nb remained in aqueous phase. Separation from hydrochloric acid solution was not possible.

RÉSUMÉ

Une méthode est proposée pour la séparation de ^{95}Zr d'avec ^{95}Nb. On procède par extraction, en solution HNO_3 2 N, au moyen d'oxyde de tri-*n*-butyl-phosphine (0.005 M dans le tétrachlorure de carbone). ^{95}Zr passe dans la phase organique, alors que ^{95}Nb reste dans a phase aqueuse.

ZUSAMMENFASSUNG

Die Trennung des ^{95}Zr von ^{95}Nb kann durch Extraktion der salpetersauren Lösung mit tri-*n*-Butylphosphinoxyd–Tetrachlorkohlenstoff erfolgen, wobei unter den angegebenen Bedingungen nur das ^{95}Zr von der organischen Phase aufgenommen wird.

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ANALYSIS OF MCPA/TBA HERBICIDE FORMULATIONS

I. A LIQUID-LIQUID CHROMATOGRAPHIC METHOD FOR DETERMINATION OF 2,3,6-TRICHLOROBENZOIC ACID

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During the last two years, a new selective herbicide has been in extensive commercial use, in cereal crops, for the control of certain weeds which are not susceptible to the long-established "hormone" weedkillers such as MCPA and 2,4D. This herbicide* is composed essentially of an aqueous solution of the alkali metal salts of trichlorobenzoic (TBA) and methylchlorophenoxyacetic (MCP) acids together with formulants added to assure satisfactory field performance. The principal physiologically active constituents of the mixture are 2,3,6-trichlorobenzoic acid and 4-chloro-2-methyl phenoxyacetic acid (4C2M) and methods were therefore required for the specific determination of these acids.

The acidic impurities in the mixture result from the manufacturing processes used for its constituent technical MCPA and technical TBA. Technical MCPA normally contains 85–100% 4C2M, the principal acidic impurities being 6-chloro-2-methyl phenoxyacetic acid (6C2M) 4,6-dichloro-2-methylphenoxyacetic acid (46C2M), 2-methylphenoxyacetic acid (2M) and the corresponding chlorinated cresols. Glycollic acid may also be present. Technical TBA usually contains a minimum of 40% 2,3,6-TBA, possible impurities (depending on the manufacturing process employed) including the 3 monochloro-acids, 6 dichloro-acids, 5 isomeric trichloro-acids, 3 tetrachloro-acids and pentachlorobenzoic acid.

The determination of 236 TBA in MCPA–TBA mixtures will be described in this part of the series. Part II describes the determination of 4C2M.

INTRODUCTION

Although the phytotoxicity of 236 TBA has been known for some time, it is only recently that commercial use has been made of its weedkilling properties. Because of this and the fact that other trichlorobenzoic acids have little commercial application, little work has apparently been carried out on the analytical chemistry, and particularly the quantitative separation, of chlorinated benzoic acids.

VELDSTRA[1] described an investigation of the U.V. spectra of some of the chlorobenzoic acids but his paper was mainly concerned with the determination of the effect of physical structure on physiological activity. It is clear from this paper that the direct determination of 236* by spectrophotometric methods will be extremely difficult, bearing in mind the complexity of technical TBA and the comparative similarity of spectra of the acids present.

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* Commercial name "Fisons 18–15".

It is probable that infra-red spectrophotometric methods could be used for the determination of 236, but in the absence of a suitable instrument at the time, it was decided to investigate partition chromatography.

The paper chromatography of chlorobenzoic acids has been described[2] and a liquid–liquid chromatographic method for separation of mono-chlorobenzoic acids is given by BHARGAVA AND HEIDELBERGER[3].

From theoretical considerations, it was expected that the di-*ortho* substituted acids would be stronger acids than their corresponding isomers. It should therefore be possible, for example, to separate 236 from 245 easily by partition between an organic solvent and a buffer solution. However, separation of, for example, 236 from 246, might be more difficult. It was thought that chromatographic separation of the MCP acids from 236 would present no difficulty.

Consequently an attempt was made to apply the experience, gained in this laboratory with liquid–liquid chromatographic methods, to the problem.

EXPERIMENTAL

Some preliminary U.V. spectrophotometric measurements were carried out on all the chlorobenzoic acids which were possible impurities. This work confirmed VELDSTRA's observations that "*ortho* substitution" appreciably reduced the molar extinction coefficient. Quantitative U.V. measurements on solutions of the chlorobenzoic acids in organic solvents enabled us to determine partition coefficients at low concentrations, between these solvents and aqueous solutions.

The first aim was to find a pair of solvents between which the partition coefficient** of 236 was about 1 : 3 to 1 : 15. To determine the effect of "polarity" of the moving phase, iso-octane, chloroform and ether were tried in separating funnel experiments involving a solvent and either a mineral acid or phosphate buffer solution.

The solubility of the acids is very low in iso-octane (236 *ca.* 2 g/l; 245 *ca.* 0.2 g/l) and the only work ever carried out with this solvent was separating funnel experiments with varying concentrations of hydrochloric acid as aqueous phase. Iso-octane and *N* hydrochloric acid gave suitable partition coefficients but the system was extremely sensitive to small changes in the acid concentration.

It was found that a suitable partition coefficient with 236 in chloroform could be obtained only by using 0.25 *M* sodium dihydrogen phosphate–phosphoric acid buffers containing a very small proportion of phosphoric acid. At this pH the buffer is not very efficient, and would probably result in asymmetric elution peaks if applied to liquid–liquid chromatography.

Ether was a slight improvement from the point of view of obtaining a suitable partition coefficient with a stable buffer, (A 12 : 1 mixture of 0.25 *M* NaH_2PO_4 and 0.25 *M* Na_2HPO_4 gave a figure of 1 : 5 for 236) and work was continued with this solvent system. In order to assess whether chromatographic separations were likely to be achieved, 245, 2356, and 26 were also examined and the approximate partition coefficients (at 0.25 mg/ml original concentration in ether and at room temperature) were 2.5 : 1, 1 : 3.3 and 1 : 11 respectively.

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* Throughout this paper these acids will be referred to by the position of their chlorine atoms (*e.g.* "236" = 2,3,6-trichlorobenzoic acid).

** All partition coefficients are expressed organic solvent: aqueous solution.

Chromatography using ether as solvent

Preliminary experiments with column chromatography were accomplished using columns 10 cm long by 9 mm diameter and prepared from 3.25 g of Celite 535* mixed with 1.6 ml of the chosen buffer. Using rather coarse kieselguhr these columns were easy to pack by MARTIN's method and gave an indication of the retention factor to be expected. The flow rate (2 ml/min) was the fastest which could be practically used with the method of detection employed (U.V. spectroscopy). Using the "12 : 1 buffer" column, 245, 2356, 236, and 26 were eluted in the predicted order, the elution volumes being, respectively, 4 ml, 6 ml, 10 ml and 14 ml.

These results showed that slightly more alkaline conditions would give better separations and exploratory columns were therefore prepared from 8 : 1 and 4 : 1 buffer solutions which indicated that 8 : 1 buffer would probably give the most satisfactory results.

Consequently, "full size" columns were prepared using a glass column 35 cm long by 1.4 cm diameter packed with 25 g of Hyflo Super-Cel containing 12.5 ml of phosphate buffer prepared from 8 vol. 0.25 *M* solution of sodium dihydrogen phosphate and 1 vol disodium hydrogen phosphate. The positions of the acids on the chromatogram derived from this column were determined spectrophotometrically in the effluent at 270 mμ. Table I shows partition coefficients of a number of acids, expected to be

TABLE I

APPROXIMATE PARTITION COEFFICIENTS OF CHLOROBENZOIC ACIDS

(Original concentration *ca.* 0.25 mg/ml ether, ether: 8 : 1 buffer solution)

Acid	*Coefficient calculated from chromatography*	*Coefficient from separating funnel experiments*
23	1 : 4.4	—
24	1 : 1.6	—
25	1 : 1.6	—
26	1 : 15	1 : 19
34	1 : 0.8	—
35	1 : 0.8	—
345	1 : 0.8	—
235	1 : 1.4	—
245	1 : 0.8	1 : 0.5
234	1 : 1.4	—
246	1 : 7.9	—
236	1 : 8.2	1 : 8.7
2346	1 : 4.7	—
2356	1 : 4.8	1 : 5.0
2345	1 : 1.5	—

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* Supplied by Johns Manville Ltd., Artillery Row, London.

present, determined by separating funnel experiments. The first column of the table shows partition-coefficients derived from chromatography. These figures are necessarily inaccurate because of the asymmetry displayed by the eluted peaks.

It was evident that 236 + 246 could be separated from the other acids. The chromatographic method was therefore applied to synthetic mixtures of chlorobenzoic acids and to technical TBA samples. The acids in the effluent fraction from the column were determined by non-aqueous titrimetry using FRITZ AND LISICKI's[3] method with 0.01 *N* sodium methylate in 6 : 1 benzene: methanol and thymol blue indicator. Analytical results were satisfactory and the method was used for some time in the routine determination of 236 + 246 in Technical TBA.

It was clear however, from asymmetry of the eluted peaks, that overloading of the columns was probably occurring resulting in occasional imperfect separation. Some improvement was achieved by increasing the pH of the buffer by reducing the ratio to 6 : 1, but a far greater improvement was found by increasing the concentration of buffer used as static phase. Buffer solutions made from 4 *M* sodium phosphate solutions were found to be impracticable because of the relatively low solubility of the sodium salts of some of the acids (*e.g.* 245 and 2356) observed in the course of separating funnel experiments. This difficulty did not arise with "2 *M*" buffers but the preparation of solutions of this concentration presented solubility problems. The potassium salt was therefore substituted for disodium hydrogen phosphate.

Table II, which shows partition ratios obtained by equilibrating 10-ml quantities of the two components of the system, illustrates the improvement achieved by a change of concentration of buffer and shows a dependence of partition ratio on concentration likely to cause trailing peaks with "0.25 *M*" buffer, whereas, although a slight concentration effect is observed with "2 *M*" buffer, the sense is reversed resulting in practically symmetrical peaks.

TABLE II

EFFECT OF CONCENTRATION ON PARTITION COEFFICIENT OF 236 BETWEEN DIETHYL ETHER AND BUFFER SOLUTIONS

Original weight of acid in mg/10 ml ether	*Partition coefficients*	
	6 : 1 "0.25 M" buffer	*1 : 1 "2 M" buffer*
0.90	1 : 30	1 : 5.0
2.25	1 : 26	1 : 6.0
4.5	1 : 21	1 : 6.2
6.75	1 : 19	1 : 7.0
9.0	1 : 17	1 : 7.5
11.25	1 : 16	1 : 7.4
13.5	1 : 15	1 : 7.2
15.75	1 : 14	1 : 8.0
18.0	1 : 13	1 : 8.4

A different ratio of phosphate solutions is required when using 2 *M* phosphate solution since concentration in the aqueous phase profoundly affects the partition coefficient and also the pH of mixture. A 1 : 1 ratio of the two 2 *M* phosphate solutions was found to be satisfactory, and has high buffer stability. Although the retention factor is lower than that with 0.25 *M* buffer, the symmetry of the eluted fraction enables satisfactory separations to be obtained.

A series of synthetic mixtures of chlorobenzoic acids was analysed using "full-size" columns (ether: "2 *M*" phosphate buffer) and typical results are given in Table III which shows that the method was reasonably accurate.

TABLE III

RECOVERIES OF CHLOROBENZOIC ACIDS USING ETHER/"2 *M*" BUFFER CHROMATOGRAPHIC COLUMNS

Acid	*Theory %*	*Percentage*		
		1	*2*	*3*
245	44.5	45.6	44.6	44.5
2356	23.7	23.1	23.9	24.2
236	31.8	31.2	31.0	31.4

Total weight of sample = 10 mg.

Chromatography using isopropyl ether as solvent

The use of ethyl ether was satisfactory under normal conditions but, during very hot weather, the high evaporation rate resulted in a number of columns giving inadequate separations. It was therefore decided to investigate an alternative solvent, and isopropyl ether was chosen. Commercially available isopropyl ether was found to be satisfactory after an initial chemical purification (distillation was avoided owing to its known hazard).

As expected, it was necessary to reduce the pH of the static phase to achieve suitable partition ratios when operating on the isopropyl ether column. A ratio of 7.5 ml of 2 *M* sodium dihydrogen phosphate to 5.0 ml of 2 *M* dipotassium hydrogen phosphate gave satisfactory results (including separation of 236 from 246) and details of the method finally adopted are given later. Fig. 1. shows the type of separation obtained.

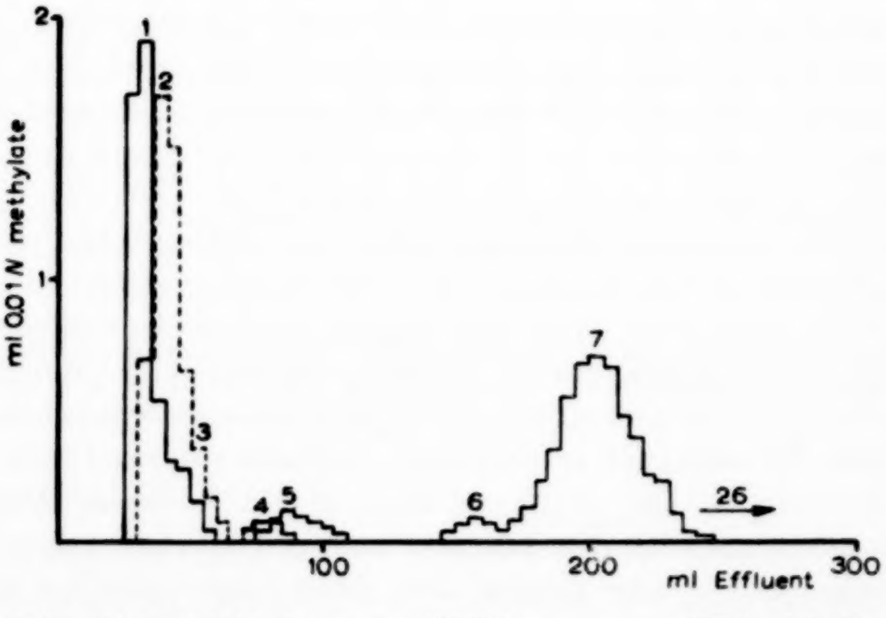

Fig. 1. Types of separation obtained: ---- MCPA; ——— TBA; (1) Mixed chlorobenzoic acids; (2) 4C2M + 46C2M; (3) 6C2M; (4) 2 *M*; (5) 23, 2346, 2356; (6) 246; (7) 236.

The first eluted acid fraction contains monochlorinated acids, 24, 25, 34, 35, 234, 235, 245, 345, 2345, and a partial separation of these constituents into two "peaks" occurs in this fraction. The second eluted acid fraction contains 23, 2346, 2356, with a slight separation of the dichloro-acid from the two tetrachloro-acids. The third eluted acid fraction contains 246 (which is usually present in very small and only just detectable quantities) and is immediately followed by the fourth acid fraction containing 236. Finally 26 is eluted.

Experiments have shown that pentachlorobenzoic acid would be eluted between 245 and 2356. This would "blur" the first separation, but since sharp separations have always been obtained with commercial TBA samples it is assumed that pentachlorobenzoic acid is not normally present. This assumption is confirmed by synthetic work which proved that pentachlorobenzoic acid was extremely difficult to prepare.

At this stage, the constituents from the technical MCPA present in the formulation were checked for elution characteristics. It was found, as predicted, that all were eluted before 236 and the position of the phenoxyacetic acids are also shown superimposed on Fig. 1. Chlorocresols precede the first chlorobenzoic acids, and glycollic acid is removed during the preliminary ether extraction of acids described in "Method".

As a final check on the qualitative validity of the proposed method, a sample of commercial formulation was chromatogrammed. The 236 fraction was compared with a solution of pure 236 by ultraviolet spectrophotometry. There was no detectable difference between the two spectra.

Titrimetry of eluted fractions

Quantitative chromatographic work, involving non-aqueous titrimetry of the eluted isopropyl ether fractions with 0.01 N sodium methylate in 6 : 1 benzene–methanol and thymol blue indicator showed that recoveries of up to 105% were obtained. The modified titration stage was therefore carefully reinvestigated using a potentiometric method of comparison.

The apparatus used was a U-shaped cell with a sintered glass disc in one of the limbs. The longer arm was half filled with a saturated solution of lithium chloride in methanol and contained a saturated calomel electrode. The other limb was two-thirds filled with a solution of the acid under examination in isopropyl ether and contained a glass electrode and a fine stainless steel needle reaching to a point just above the sintered glass disc. Nitrogen was led in through this needle and the glass electrode was placed as close as was practicable to the sintered glass disc. The pH meter used was checked for grid current on the input valve and although the whole apparatus was shielded electrically it was necessary to avoid external electrical interference.

Experiments were carried out using four typical acids present in commercial TBA (26, 245, 236, 2356). The potentiometric titration of these acids immediately showed that the colour change of the indicator used in previous work was not coincident with the inflection point. Examination of numerous indicators showed that bromothymol blue gave better results on the 5-ml scale used. It did, however, demonstrate that some shift of colour change with this indicator occurred with increasing concentration of titrant. A change to a similar titrant with dried isopropyl ether substituted for benzene was found to diminish but not eliminate the effect and the poor solubility of bromothymol blue in isopropyl ether, rendered some fractions untitratable. An immediate benefit was found by adding sufficient methanol to the eluent to match the composition of the titrant solvent and the colour changes were then found to be coincident with inflection points at concentrations of the four acids ranging from 1–6 mg/5 ml of eluent solution.

It was proposed to use benzoic acid as a primary standard for sodium methylate titrant, so this acid was also tested in a similar way. It was found to give an inflection point at the colour change of bromothymol blue within the same range of concentration as the acids investigated above. It suffers from the slight defect of low solubility of the sodium salt in the titrant but this did not influence the accuracy of standardisation.

Diethyl ether was used as a convenient solvent for the prepared sample (for chromatography or determination of "total acidity") and for benzoic acid for standardisation. The small quantity of diethyl ether used was shown not to affect the accuracy of the end-point and this solvent had the advantage of higher solvent power for the acids. The blank in all cases was negligible.

The use of bromothymol blue is, as noted above, complicated by the low solubility of the indicator in isopropyl ether and, in the case of the fractions of large volume, the original indicator, thymol blue, was retained because, although the results were slightly in error, the quantities of 26 (the only acid titrated in large volumes) present in commercial formulations are usually small enough to render this error negligible.

METHOD

Apparatus

The chromatograph tube consists of 35 cm of glass tube of 14 mm i.d., the lower end reduced to 5 mm i.d., and with a B.19 socket at the upper end fitted with ears for retaining springs below the joint. The solvent is contained in a tap funnel provided with B.19 joints at top and bottom and with ears to mate up with the corresponding ears on the tube. A 5- or 10-ml microburette calibrated in 0.01-ml divisions is used for the titrant: 1-ml pipette graduated between two marks.

Reagents

All reagents of analytical reagent grade unless otherwise stated.

Benzoic acid; dilute hydrochloric acid (1 : 1); diethyl ether (laboratory reagent grade); sodium sulphate (anhydrous); nitrogen.

Prepared kieselguhr

Allow Hyflo Super-Cel* to stand overnight under concentrated hydrochloric acid, wash with water until the washings are neutral to litmus and dry at 100–110° in an oven.

Equilibrated isopropyl ether (moving phase)

Wash technical isopropyl ether (Shell Chemical Co.) twice with 1 *N* sodium hydroxide solution and successively with water until the washings are neutral to litmus.

Buffer solution

(*A*) potassium hydrogen phosphate 2 *M*; (*B*) sodium dihydrogen phosphate 2 *M*.

Mix in proportions 1 volume of *A* and 1.5 volume of *B* and shake with an equal volume of equilibrated isopropyl ether before use.

Preparation of the column

Weigh 25 g of prepared Hyflo Super-Cel into a mortar. Add dropwise from a graduated pipette with stirring, 12.5 ml of buffer solution. Triturate gently but thoroughly to homogenize the Hyflo Super-Cel buffer mixture. Add sufficient equilibrated isopropyl ether to form a thin slurry and mix well. Having plugged the bottom of the column with a small wad of ether-extracted cotton wool, pack the slurry into the column, with a perforated disc plunger using MARTIN's[4] method. The length of a normal column is about 30 cm. Wash through with about 50 ml of equilibrated isopropyl ether using an applied pressure, at 2.5–3 ml/min.

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* Supplied by Johns Manville Ltd., Artillery Row, London.

Titrant (0.01 N sodium methylate in isopropyl ether)

Dissolve 2.5 g of metallic sodium in 100 ml of methanol (purified by distillation from potassium hydroxide), cool and add to 800 ml of dried isopropyl ether (washed with sodium hydroxide and dried over sodium sulphate followed by sodium). Add a further 100 ml of purified methanol. This produces an approximately 0.1 *N* "stock titrant" which should be allowed to stand 2–3 days before use. It should be kept in a bottle and protected from carbon dioxide.

To prepare the 0.01 *N* sodium methylate, mix 400 ml of purified and dried isopropyl ether with 100 ml of purified methanol. Pass nitrogen through for 15 min. Add 50 ml of 0.1 *N* "stock titrant" (carefully pipette to avoid any deposit and to avoid absorption of carbon dioxide) and continue passing nitrogen in order to mix thoroughly. The 0.01 *N* solution should be protected from atmospheric carbon dioxide. The method of standardisation is given below.

Indicator (1)

Dissolve 0.1 g of bromothymol blue in 50 ml of purified methanol. Pass nitrogen through this solution and add sufficient "stock titrant" to convert the indicator to the green form. Add this solution to 1 l of purified methanol which has had carbon dioxide removed by bubbling purified nitrogen through it for 15 min. This solution should be stored in a bottle equipped with suitable dispensing devices incorporating means for the exclusion of atmospheric carbon dioxide.

Indicator (2)

Dissolve 0.4 g of thymol blue in 100 ml of purified methanol and add sufficient "stock titrant" to give the neutral colour.

Standardisation of titrant

Weigh out accurately about 0.5 g of benzoic acid. Dissolve in diethyl ether and make up to 100 ml in a volumetric flask after adjusting the temperature to 20°. Pipette, at 20°, a 1-ml aliquot into a clean dry test tube (*Note 1*, p. 279), pass nitrogen for 1 minute and titrate with 0.01 *N* methylate using 1 ml of indicator (1) to the green colour of the indicator. Repeat the standardisation at least twice. If W_s is weight of benzoic acid used and t_s is the titre:

$$\text{Normality} = 8.19\,\frac{W_s}{t_s} \times 0.01\ N$$

PROCEDURE

(1) Preparation of sample

Weigh accurately sufficient sample to contain 1.8–2.2 g (*Wg*) of acids. Dilute to 60–80 ml with distilled water and add, with good agitation, sufficient 1 : 1 hydrochloric acid to make the solution definitely acid. Extract with 3 × 30-ml of diethyl ether, combine the solvent extracts and wash with 2 × 10-ml portions of distilled water. Combine the water washings and shake them with 10 ml of ether. Combine all the ether extracts, dry with sodium sulphate and make up accurately to 200 ml with diethyl ether after adjusting the temperature to 20°. This is the stock solution. It should be used at 20° and evaporation losses should be avoided.

(2) *Determination of "total acids" content of stock solution*

Pipette 1 ml of stock solution at 20° into a test tube (*Note 1*). Pass nitrogen through for 1 min and titrate with 0.01 *N* titrant using 1 ml of indicator (1) to the green colour. If t = ml of 0.0100 *N* methylate consumed, f = factor of titrant, then the "total acids" content (expressed as TBA):

$$= \frac{45.1t}{W} \text{ \% w/w.}$$

(3) *Determination of 2,3,6-trichlorobenzoic acid*

Apply nitrogen pressure to the top of the column until the moving phase just falls to the level of the kieselguhr packing. Release the pressure and pipette (*Note 1*, p. 279) 1 ml of stock solution at 20° on to the top of the column and force the ether layer down to the top of the packing. Wash down the sides of the column with 2 ml of moving phase and again apply pressure to the top of the column until the solvent has fallen to the level of the kieselguhr. Repeat this operation. Fill the reservoir, fit to the top of the column and apply sufficient pressure to produce a flow rate of 2 ml/min. Collect 60 × 5-ml fractions followed by 2 × 100-ml fractions. Pass nitrogen for 1 min through each 5-ml fraction and titrate to the green colour with 0.01 *N* methylate titrant using indicator (1). Pass nitrogen for 2 min through each 100-ml fraction and titrate to the grey colour with 0.01 *N* methylate using indicator (2). The resultant titres will fall into five groups (*Notes 2* and *4*).

Fractions 1–4: These contain no significant titratable acids since they represent the dead volume of the column.

Fractions 5–12: These fractions contain the chlorobenzoic acids except 23 and the di-*ortho* substituted acids together with all the MCP acids.

Fractions 13–27: These fractions contain 2356, 2346, and 23.

Fractions 28–60: These fractions contain 246 and 236 which are usually separated (*Note 3*).

Fractions 61–62 (100 ml): These fractions contain 26.

Calculation of "active" (236 content)

The titres in group 4 fall into two distinct fractions resolved or resolvable by inspection. The second and major fraction is 236. If titre of 236 fraction in ml 0.01000 *N* methylate = t ml, then

$$\text{\% 236 in sample} = \frac{45.1t}{W} \text{ \% w/w}$$

Notes

1. It is important that the same pipette is used for standardisation, determination of "total acids" and chromatography. Considerable care should be taken during pipetting operations, to avoid loss of isopropyl ether by "creeping" or evaporation. Care should also be taken to avoid errors due to temperature changes (isopropyl ether has a relatively high coefficient of expansion).

2. The distribution of the acids on the column is slightly dependent on packing technique. The numbers of fractions shown should be taken as a guide, as slight variations in position may occur from column to column. It is preferable to run a synthetic sample or known commercial sample to check the column before analysing an unknown.

3. The efficiency of column varies somewhat with the skill of the operator packing the column. In our experience all columns achieve satisfactory separations into the five "groups" indicated, but columns sometimes fail to separate 236 and 246 completely in "group 4". 246 is usually present in small quantities (up to 5% of the 236 content) and even when a complete separation is not achieved, an approximation can usually be made which is accurate enough for most practical purposes.

4. With some commercial samples, it has been found that the sum of the fraction titres does not equal the amount predicted from the "total acid" content of the stock solution. This is due to the presence of small quantities of unidentified acids which are not eluted from the column until after the 26 and in some cases are retained on the column. For this reason it is inadvisable to use columns for more than two determinations on certain commercial samples.

DISCUSSION

The partition coefficients of the acids, using the isopropyl ether/"2 *M*" buffer system finally adopted, have not been determined directly by separating funnel experiments, but practical column experiments show that there is little difference in the relative positions of acids when compared with the ether/"0.25 *M*" buffer system which was investigated earlier. The partition data of typical acids calculated from column performance using the adopted method is given in Table IV.

TABLE IV

PARTITION COEFFICIENT OF TYPICAL CHLOROBENZOIC ACIDS CALCULATED FROM COLUMN MEASUREMENTS

Acid	*Partition coefficient*
245	1 : 0.8
2356	1 : 4.8
236	1 : 14.0

The partition isotherms of the acids were still virtually linear so that symmetrical peaks were obtained.

Chromatographic analyses of standard solution of pure acids have been carried out and the results obtained confirm the accuracy expected from the potentiometric study. Since the "p*K* values" of other possible acidic impurities are unlikely to differ appreciably from those tested it was assumed that the titration technique was valid for commercial formulations. Results obtained on a mixture of pure TBA acids are given in Tables V and VI.

TABLE V

RECOVERIES OF CHLOROBENZOIC ACIDS USING ISOPROPYL ETHER/"2 *M*" BUFFER CHROMATOGRAPHIC COLUMNS

Acid	*Added*	*Found*					
		1	*2*	*3*	*4*	*5*	*6*
245	41.5	41.4	41.4	41.6	41.2	42.8	42.4
2356	17.5	18.0	18.0	18.4	18.1	17.4	17.1
236	41.0[a]	40.4	40.4	40.1	40.6	39.8	40.5

[a] Total weight of sample is 10 mg. The 236 acid was shown chromatographically to contain *ca.* 1% of 2356.

TABLE VI

DETERMINATION OF 236 IN PRESENCE OF TECHNICAL MCPA

MCPA present (4C2M)	*236 present g/l*	*236 found g/l*	
100	48	48.5	48.8
100	24	23.7	24.3
50	48	49.2	48.5
50	96	97.0	96.6

ACKNOWLEDGEMENTS

The authors would like to thank G. F. LAWS and H. G. HAYNES for synthesising most of the chlorobenzoic acids used in checking the method, and the directors of Fisons Pest Control Limited for permission to publish this paper.

SUMMARY

A liquid–liquid partition chromatographic method has been developed for the determination of 2,3,6-trichlorobenzoic acid in MCPA/TBA herbicides. The system used is isopropyl ether–phosphate buffer and eluted acid fractions are titrated in non-aqueous solution with sodium methylate solution. The effect of all possible chlorobenzoic acid and methyl chlorophenoxyacetic acid impurities has been investigated. A precision of about ± 2% is applicable to the method.

RÉSUMÉ

Une méthode chromatographique a été mise au point pour le dosage de l'acide trichloro-2,3,6-benzoïque dans des herbicides. On effectue un titrage de l'éluat, en solution non aqueuse, au moyen de méthylate de sodium.

ZUSAMMENFASSUNG

Beschreibung einer chromatographischen Methode zur Bestimmung von 2,3,6-Trichlorbenzoesäure in Herbiciden durch Titration mit Natriummethylat in nicht-wässrigem Medium.

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THE DIRECT DETERMINATION OF URANIUM IN CONCENTRATES BY SPECTROPHOTOMETRIC TITRATION WITH FERRIC SULPHATE

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INTRODUCTION

Methods most widely used at present for the determination of large amounts of uranium involve reduction of uranium to the +4 state with metallic reductors such as lead, zinc or cadmium, followed by titration with ceric sulphate, potassium dichromate or sodium vanadate[1]. These methods, however, may not be directly applied to uranium concentrates, since several elements, particularly iron, interfere seriously. For this reason a preliminary separation of uranium is usually carried out. The determination may be made much more selective by the use of a milder agent, such as bismuth metal or amalgam for reduction of uranium, and a milder oxidant, such as ferric sulphate, for titration of the reduced solution. Under these conditions the only common interfering elements are those which induce the atmospheric oxidation of uranium(IV)[2]. This may be controlled to some extent by carrying out the reduction and titration under nitrogen.

The titration of uranium(IV) with iron(III) is usually carried out at 90°, and the end-point detected potentiometrically[3,4]. Titration at this high temperature is inconvenient, and the danger of atmospheric oxidation is greatly increased. It is shown in this paper that high temperatures are necessary only for the rapid establishment of equilibrium potentials at the indicator electrode, since in dilute sulphuric acid solution at room temperature the oxidation of uranous ions by ferric ions is very rapid. This reaction has previously been investigated spectrophotometrically[5,6], and amperometrically at the dropping mercury electrode[5].

A procedure for the determination of uranium in concentrates is described in this paper, in which reduction is carried out under nitrogen with bismuth amalgam, and the reduced solution is titrated spectrophotometrically with ferric sulphate in a nitrogen atmosphere. Copper, molybdenum and vanadium interfere to some extent, but are not usually present in Australian uranium concentrates in sufficient amounts to cause serious error. A complete determination may be carried out in about 70 min, with a precision of 2 to 3 parts per thousand.

Apparatus

Spectrophotometer: A Hilger "Uvispek" was used without modification. A carriage for the titration cell was constructed from perspex, and shaped to fit in the position of the normal cell carriage. A raised cover for the cell compartment was also made of perspex. Three holes were drilled in the cover, two for nitrogen tubes, and one for the burette tip. Both the cover and the cell carriage were painted matt black.

Titration cell: This is shown in Fig. 1. The T-shaped titration cell had two flat, circular windows cemented to the body of the vessel, and a light path of about 3 cm. The nitrogen inlet and outlet connecting tubes were Nylex, painted matt black, and closed at the ends by stopcocks. Nitrogen was used both to stir the solution and to exclude oxygen. The burette port of the titration cell was closed by a small serum cap.

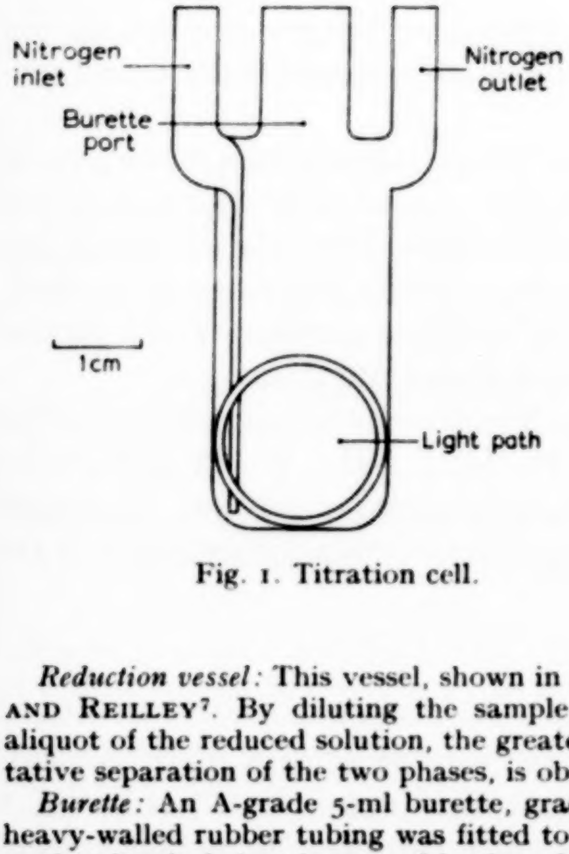

Fig. 1. Titration cell.

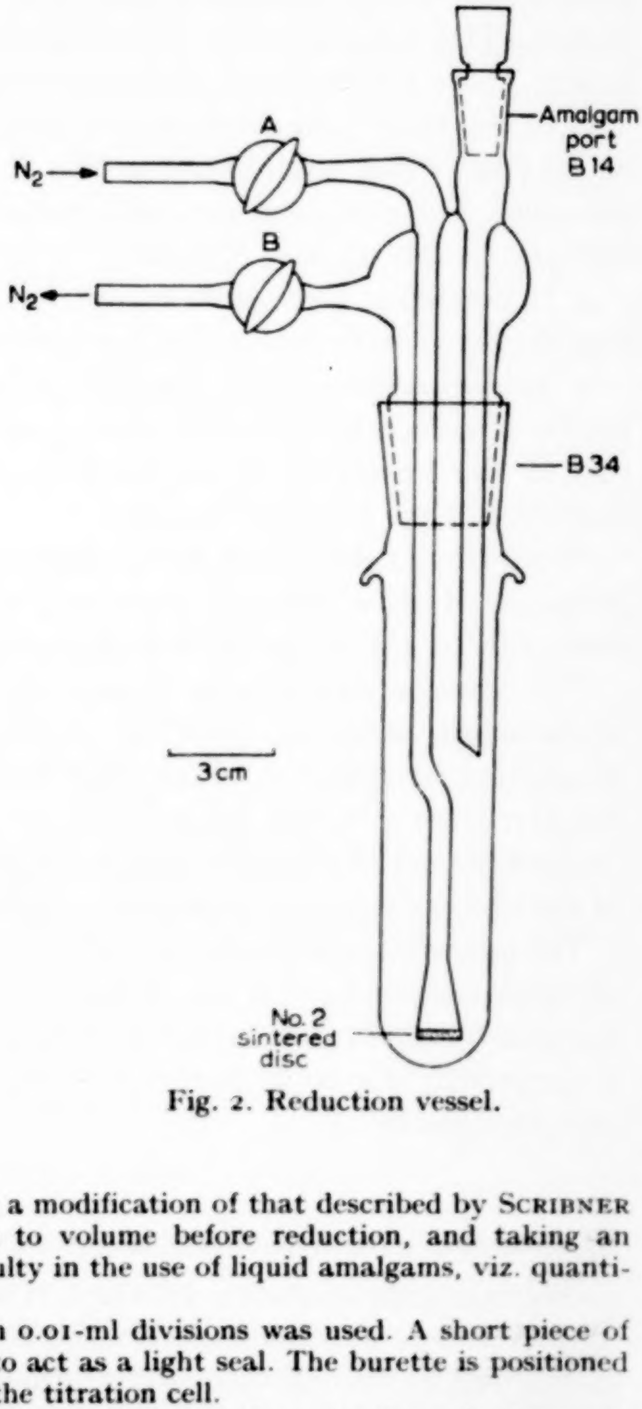

Fig. 2. Reduction vessel.

Reduction vessel: This vessel, shown in Fig. 2, is a modification of that described by SCRIBNER AND REILLEY[7]. By diluting the sample solution to volume before reduction, and taking an aliquot of the reduced solution, the greatest difficulty in the use of liquid amalgams, viz. quantitative separation of the two phases, is obviated.

Burette: An A-grade 5-ml burette, graduated in 0.01-ml divisions was used. A short piece of heavy-walled rubber tubing was fitted to the tip to act as a light seal. The burette is positioned so that its tip is just immersed in the solution in the titration cell.

Cathode ray polarograph: A linear-sweep cathode ray polarograph from Southern Instruments Computer Division, England, was used for the oxidation-rate studies.

The uranous–ferric reaction

There is some confusion in the literature regarding the rate of oxidation of uranous ion by ferric ion. Several authors[3,8,9] have reported the reaction,

$$U(IV) + 2\ Fe(III) \rightarrow U(VI) + 2\ Fe(II)$$

to be very slow at room temperature. Others[5] have suggested that the reaction is rapid if carried out in a suitable medium.

In order to determine the optimum conditions for the titration of uranium(IV) with iron(III) at room temperature, the reaction was studied in sulphuric, hydrochloric and perchloric acid solutions, using spectrophotometry and cathode ray polarography. The uranium(IV) concentration may be followed on a spectrophotometer by utilizing the sharp absorption peak of U(IV) at 650.0 mμ, and both the uranium(VI) and iron(III) concentrations at any instant may be determined by cathode ray polarography. These two separate techniques showed that:

1. In sulphuric acid solutions less than 1 *N* acid, the reaction at 20° is very rapid, equilibrium being established in less than 10 sec even when the titration is 80% complete. The rate decreases with increasing acid concentration, but the titration is still practicable up to 5 *N* H_2SO_4.

2. In perchloric acid solutions the reaction is slower than in sulphuric acid, and the rate decreases with increasing acid concentration.

3. In hydrochloric acid solutions at room temperature the oxidation of uranous ion by ferric ion is extremely slow, even at low acid concentrations. This is probably due to the formation of an iron(III)-chloro complex, which lowers the standard potential of the Fe^{+2}/Fe^{+3} system.

These results show that dilute sulphuric acid is the most suitable medium for the proposed titration. The end-point may be detected spectrophotometrically or amperometrically at the dropping mercury electrode.

The titration may also be carried out in 0.5 *N* H_2SO_4 at room temperature using amperometry with two polarised platinum electrodes ("dead-stop" end-point), and an applied potential of 10 mV. The titration is rather slow before the end-point, but the first trace of excess ferric ion causes an immediate steady galvanometer reading. Oxygen should be excluded during the titration by bubbling nitrogen. The detection of the end-point is not as precise as by spectrophotometric titration.

The following potentiometric indicator systems did not give a satisfactory end-point at room temperature in 0.5 *N* H_2SO_4: S.C.E. – Pt, S.C.E. – Hg, W – Pt and Pt – Pt (polarized 1.5 μA). The failure of these potentiometric systems to detect the end-point is apparently due to sluggishness in the setting up of an equilibrium potential at the indicator electrode.

Spectrophotometric detection of end-point

The spectrophotometric titration of uranium(IV) with ferric ammonium sulphate may be followed either by utilizing the sharp absorption peak of U(IV) at 650 mμ[5], or the Fe(III) wave at 350 mμ[6]. Uranium(IV) in sulphuric acid solution obeys Beers' law over the concentration range studied, and has a molar absorptivity of 42 at 650 mμ. This is a convenient sensitivity for the conditions of the determination, and, moreover, the molar absorptivity remains constant over a sulphuric acid concentration range of at least 1–7 *N*. It is also advantageous to work in the visible region if the spectrophotometer is to be used for other routine estimations. Uranyl, ferrous and ferric ions in sulphuric acid solution have molar absorptivities of less than one at 650 mμ.

In order to minimize induced oxidation of uranium during the titration, a relatively high acidity, 3.5 *N*, was used. At this concentration of sulphuric acid the reaction is rather slow in the vicinity of the end-point, and readings are not taken in this region.

A typical titration plot is shown in Fig. 3. A titration may be carried out in 15 min.

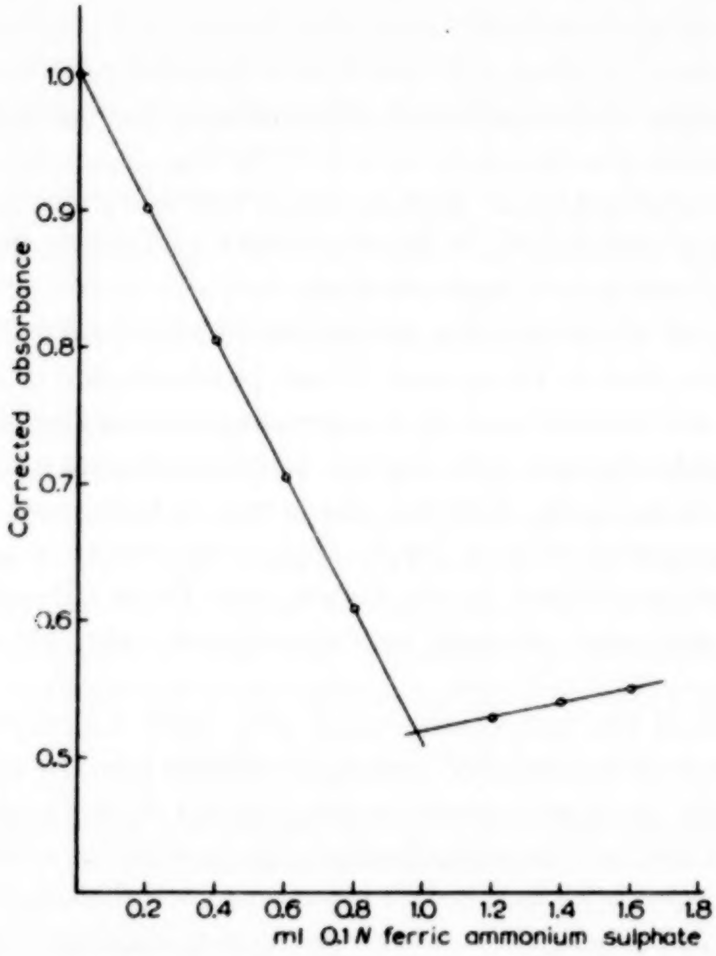

Fig. 3. Spectrophotometric titration of uranium(IV) with ferric sulphate.

Reduction of uranium with bismuth amalgam

The reduction of uranyl ion by bismuth amalgam may be represented by:

$$3\ UO_2^{+2} + 2\ Bi + 8\ H^+ \rightleftharpoons 3\ U^{+4} + 2\ BiO^+ + 4\ H_2O$$

Conditions for the reduction are therefore favoured by high sulphuric acid concentrations[10,11]. A shaking time of over an hour is required for complete reduction in 3 *N* H_2SO_4, 20 min in 5 *N* H_2SO_4 and 5 min in 7 *N* H_2SO_4. Reduction proceeds only to the +4 state in 7 *N* sulphuric acid. Very little reaction occurs in perchloric acid solutions of any concentration.

If large amounts of oxidizing agents are present in the sample solution, they should be removed by a preliminary reduction with hydroxylamine sulphate.

EXPERIMENTAL

Reagents

Bismuth amalgam: Add 20 g of reagent grade granular bismuth to 900 g of pure mercury. Cover the mixture with 1 *N* sulphuric acid and warm and stir until dissolved. Cool to room temperature, then wash the amalgam well with water. Transfer to a separatory funnel, and allow the liquid portion of the amalgam to drain into a second funnel containing 1 *N* sulphuric acid. Store the amalgam in this funnel and run off as needed.

0.1 N ferric ammonium sulphate: Dissolve 12 g of reagent-grade material in 3.5 *N* sulphuric acid.

Dilute to 250 ml with 3.5 *N* H_2SO_4. Standardize against pure, dry U_3O_8, using the procedure outlined.

Nitrogen: Commercial nitrogen containing less than 5 v.p.m. of oxygen was used without further purification.

Procedure

Weigh a dried sample of the concentrate containing 50–100 mg U_3O_8 into a small flask. Dissolve by heating with 10 ml of 2.5 *N* $HClO_4$. Evaporate to fumes of $HClO_4$ to dehydrate silica, and continue heating until the silica is colorless. Dilute with water, filter, and wash with hot 0.1 *N* H_2SO_4. Add 5 ml of conc. H_2SO_4 to the filtrate, cool, and dilute to 25 ml in a volumetric flask.

Transfer about 15 ml of the solution to the dry reductor tube. Insert head of vessel and connect nitrogen source. Open cock A and pass nitrogen at a moderate rate for 1 min. Close cock A and simultaneously remove stopper from amalgam port. Add 2 ml bismuth amalgam with nitrogen still flowing. Replace stopper and open cock A. Close cocks A and B simultaneously. Remove the nitrogen tube, and clamp the reductor in the arm of a wrist-action shaker. Shake vigorously for 5–10 min. Pipette 5 ml of water into the titration cell and fit the serum cap. Place the cell in position in the spectrophotometer and pass nitrogen at a convenient rate. Set the wave length at 650 mμ.

Remove the head of the reduction vessel and, with a dry pipette, immediately transfer a 5-ml aliquot of the reduced uranium solution into the titration cell, through the serum cap. Insert the 5-ml burette containing 0.1 *N* ferric ammonium sulphate. Zero the instrument and set the absorbance scale reading at a convenient value, say 1.000. Close the nitrogen inlet and outlet taps, and with the selector switch on "measure", open the slit and adjust the "check" position to balance. Close the slit and pass nitrogen. Add the first increment of the titrant. Interrupt nitrogen flow, open slit and measure absorbance. Close slit, start nitrogen and add second increment of titrant. Repeat this procedure until a full titration curve is obtained. Correct each absorbance reading for the dilution effect, and plot corrected absorbance *versus* titre.

Study of interferences

Using the procedure described above, the following elements, when present in equal concentration to uranium (wt. %), did not interfere in the spectrophotometric titration:

Ce, Co, Cr, Fe, Ni, P, Sb, Sn, Ti and W.

Copper, molybdenum and vanadium interfered to varying degrees, and were studied in more detail.

Copper: Copper is notorious for its ability to induce the air-oxidation of uranium(IV)[2]. Slightly low results were obtained in the spectrophotometric titration even when extreme measures were taken to exclude oxygen from the titration cell. The error is approximately proportional to the copper concentration. The maximum permissible copper content, for an error of less than 2 parts per thousand, is 3% of the uranium concentration. Since uranium concentrates processed in this country usually contain less than 0.2% copper, this limit is not likely to be exceeded.

Molybdenum: In the presence of oxygen, molybdenum causes low results in the titration of uranium with ferric sulphate. If oxygen is excluded, however, slightly high results are obtained. This is possibly due to the formation of traces of molybdenum (III) in the bismuth reductor. Molybdenum may be tolerated up to 2% of the uranium concentration.

Vanadium: Vanadium, like copper and molybdenum, induces the air-oxidation of uranium(IV). Vanadium is reduced only to the +4 state by bismuth amalgam in 7 *N* sulphuric acid. The maximum permissible vanadium content is 5% of the uranium concentration.

The presence of large amounts of ferrous iron, while not affecting the final result, causes the spectrophotometric titration in 3.5 *N* H_2SO_4 to be inconveniently slow. When analysing ores, where the iron content usually exceeds the uranium content, the sulphuric acid should not be more than 0.5 *N* during the titration.

Analysis of concentrates and high-grade ores

Table I shows the results obtained by the direct spectrophotometric titration on five standard uranium concentrates, and two standard high-grade ores. The concentrates were analysed by an independent laboratory using the classical method consisting of a cellulose column separation of uranium from nitric acid–ether solution, followed by precipitation with ammonia and ignition to U_3O_8. The uranium content of the ores was determined by cathode ray polarography after a mercury cathode separation[12].

TABLE I

DETERMINATION OF URANIUM IN CONCENTRATES AND ORES BY SPECTROPHOTOMETRIC TITRATION WITH FERRIC SULPHATE

Sample No.	*Direct spectrophotometric titration % U_3O_8*	*Number of determinations*	*Relative standard deviation(n–1)%*	*Reference method % U_3O_8*
C1	64.8	6	0.35	64.55
C2	63.1	6	0.19	63.35
C3	71.9	6	0.20	72.00
C4	23.90	4	0.33	23.90
C5	24.48	4	0.28	24.55
ore 1	8.33	3	0.54	8.3
ore 2	7.52	3	0.67	7.6

SUMMARY

A direct method is presented for the determination of uranium in concentrates by spectrophotometric titration with ferric sulphate, after a bismuth amalgam reduction. The oxidation of U(IV) by Fe(III) was found to be rapid and complete at room temperature, under suitable conditions. Copper, molybdenum and vanadium interfere to some extent, and their maximum permissible concentrations are discussed. A complete determination may be carried out in little over an hour with a precision of 2–3 parts per thousand. An Uvispek spectrophotometer was adapted for spectrophotometric titrations without modification of the instrument.

RÉSUMÉ

Une méthode est proposée pour le dosage de l'uranium. On procède par titrage spectrophotométrique de l'uranium(IV) au moyen de sulfate ferrique. L'uranium(IV) est obtenu par réduction au moyen d'un amalgame de bismuth.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Uran in Konzentraten durch spektrophotometrische Titration mit Eisen(III)-sulfat nach Reduktion mit Wismutamalgam.

Anal. Chim. Acta, 23 (1960) 282–288

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AUTOMATIC DERIVATIVE SPECTROPHOTOMETRIC TITRATION OF EXCESS EDTA IN THE DETERMINATION OF COBALT, COPPER OR IRON

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EDTA has been used for the determination of copper, iron and cobalt, and metal indicators have been applied to the end-point detection, in both direct titration or back-titration procedures[1]. However, the intense colors of EDTA complexes formed by these metals limit their determination to only a few milligrams. Lately Wilkins[2] introduced a class of metal indicators, "the metalfluorechromic indicators," which can be applied to the chelometric titration of macro amounts of metals yielding highly colored EDTA complexes. Wilkins used Calcein W as a visual fluorescence indicator in the determination of cobalt, iron, copper, chromium, and nickel in a back-titration procedure. The titrations were carried out in a dark enclosure under ultraviolet illumination, and the end-point for titration of excess EDTA was observed as a quenching of the green fluorescence of the free indicator.

Recently the authors described an automatic titration method for the determination of calcium and magnesium[3], which uses the automatic derivative spectrophotometric end-point detection system provided in the "Spectro-Electro" titrator[4]. The same method is well suited for both macro and micro automatic titration methods for copper, iron, and cobalt. Calcein W is used as an absorption indicator for the automatic end-point and as a fluorescence indicator to signal the presence of excess EDTA prior to back titration.

CHARACTERISTICS OF THE METHOD

A beaker of sample solution is inserted into the "Spectro" titrator, Calcein W indicator is added, and standard EDTA added until in excess, as indicated by a definite appearance of a green fluorescence. The fluorescence is easily observed visually from the illumination by the incident beam from the tungsten source in the "Spectro" unit. The small excess of EDTA is then automatically titrated in a few seconds with a standard copper solution using the same Calcein W as an absorption indicator. At the end-point a rapid increase in absorbance occurs at about 500 mμ when the last traces of free indicator are tied up with the copper. This absorbance change produces an end-point signal for automatic termination of the titration. The properties of Calcein W to both fluoresce and absorb in the visible and not to be blocked by copper, iron or cobalt make it advantageous over other metal indicators.

The absorption curves of the species present in the titration of copper, at the beginning of the back-titration, and of those present at the automatic end-point, at pH 4.4, are given in Fig. 1. Similar curves are given for iron in Fig. 2 and for cobalt in Fig. 3. The absorption curves of free Calcein W and those of EDTA complexes of copper, iron, and cobalt are given in Fig. 4.

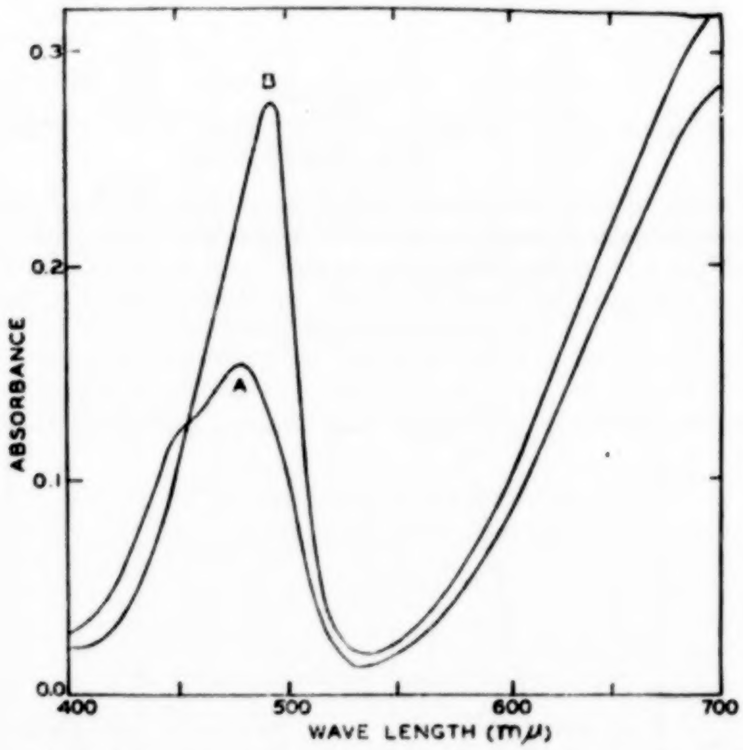

Fig. 1. Absorption spectra of copper complexes and free Calcein W. A. Cu-EDTA + Cu-Calcein W + excess EDTA + free Calcein W curve, $3.3 \cdot 10^{-3}$ M Cu-EDTA, $0.7 \cdot 10^{-3}$ M EDTA, 0.00015% Calcein W, buffered at pH 4.4, at the beginning of the back-titration. B. Cu-EDTA + Cu-Calcein W curve, $4 \cdot 10^{-3}$ M Cu-EDTA, buffered at pH 4.4, at the automatic end-point.

It can be seen from Figs. 1, 2 and 3, that at 500 mμ, the difference in absorbance between the absorbing species present at the beginning of the back-titration and those present at the automatic end-point is about the same, 0.14 of an absorbance unit for about 13 mg of copper, iron or cobalt in a volume of 60 ml. The relative change in absorbance becomes smaller as the concentration of metal increases, because the

EDTA complexes of copper, iron, and cobalt also absorb somewhat at 500 mμ (see Fig. 4).

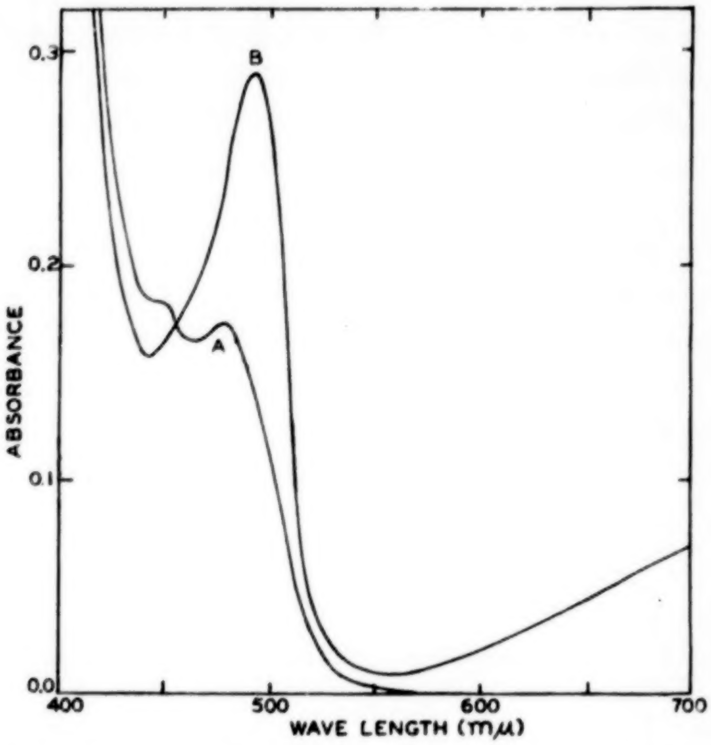

Fig. 2. Absorption spectra of iron complexes and free Calcein W. A. Fe-EDTA + Fe-Calcein W + excess EDTA + free Calcein W curve, $3.3 \cdot 10^{-3}$ *M* Fe-EDTA, $0.7 \cdot 10^{-3}$ *M* EDTA, 0.00015% Calcein W, buffered at pH 4.4, at the beginning of the back-titration. B. Fe-EDTA + Cu-EDTA + Cu-Calcein W curve, $3.3 \cdot 10^{-3}$ *M* Fe-EDTA, $0.7 \cdot 10^{-3}$ *M* Cu-EDTA, buffered at pH 4.4, at the automatic end-point.

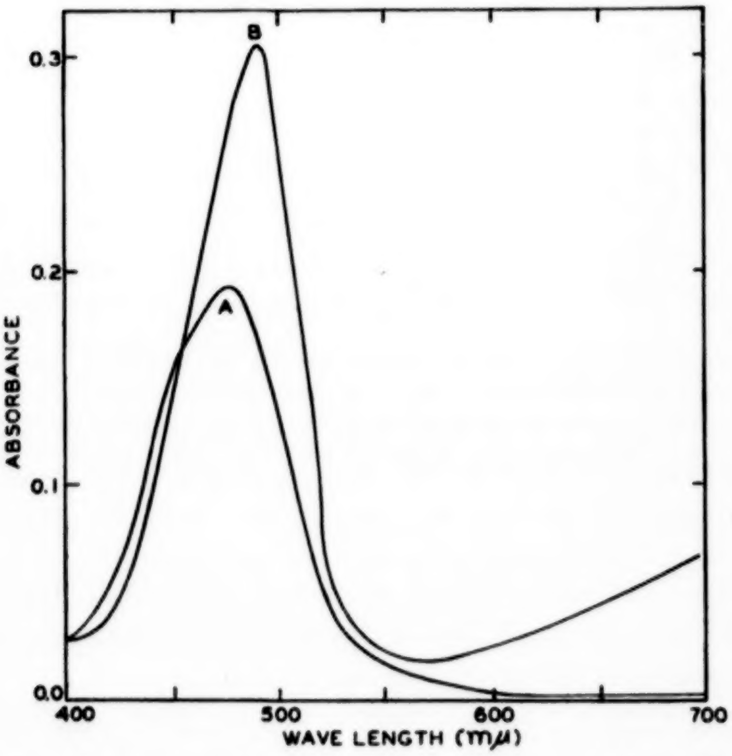

Fig. 3. Absorption spectra of cobalt complexes and free Calcein W. A. Co-EDTA + Co-Calcein W + excess EDTA + free Calcein W curve, $3.3 \cdot 10^{-3}$ *M* Co-EDTA, $0.7 \cdot 10^{-3}$ *M* EDTA, 0.00015% Calcein W, buffered at pH 4.4, at the beginning of the back-titration. B. Co-EDTA + Cu-EDTA + Cu-Calcein W curve, $3.3 \cdot 10^{-3}$ *M* Co-EDTA, $0.7 \cdot 10^{-3}$ *M* Cu-EDTA, buffered at pH 4.4, at the automatic end-point.

Recorded titration curves for copper, iron, and cobalt are shown in Fig. 5. It is seen that the change in voltage output for iron and cobalt decreases as the amount of metal titrated increases. However the rate of change in output voltage during a titration is a maximum at the equivalence point and sufficient to ensure an automatic end-point.

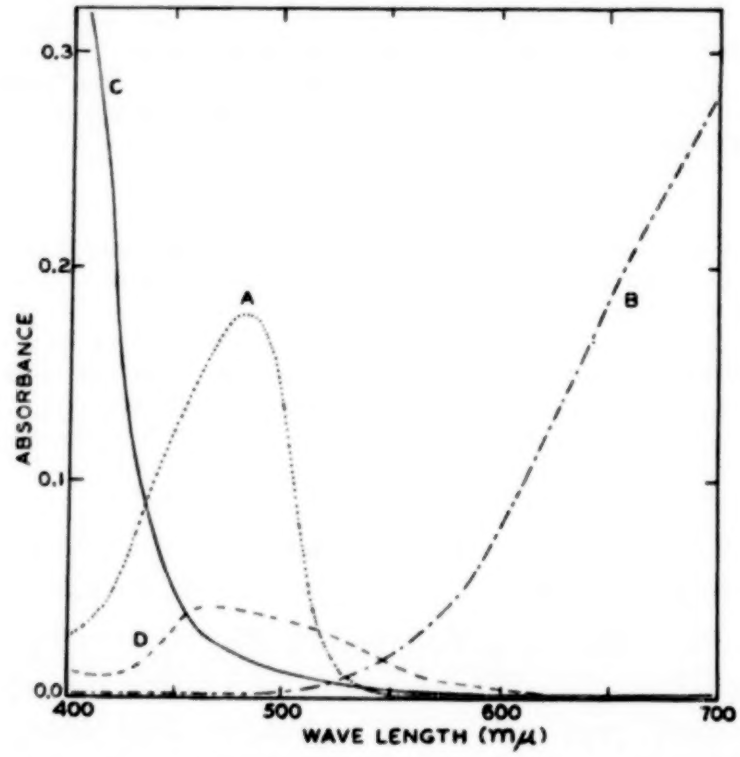

Fig. 4. Absorption spectra of free Calcein W, Cu-EDTA, Fe-EDTA, and Co-EDTA complexes. A. Calcein W curve, 0.00015% Calcein W buffered at pH 4.4. B. Cu-EDTA curve, $3.3 \cdot 10^{-3}$ *M* Cu-EDTA, buffered at pH 4.4. C. Fe-EDTA curve, $3.3 \cdot 10^{-3}$ *M* Fe-EDTA, buffered at pH 4.4. D. Co-EDTA curve, $3.3 \cdot 10^{-3}$ *M* Co-EDTA, buffered at pH 4.4.

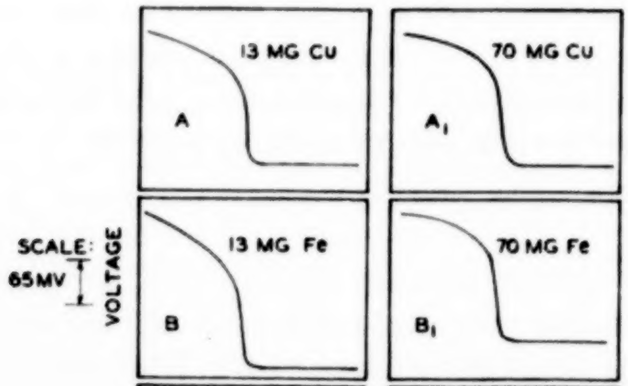

Fig. 5. Recorded curves from output of detector circuit for the EDTA back-titration of copper, iron and cobalt with Calcein W as indicator and copper as titrant. A and A_1. Copper + Calcein W at pH 4.4. B and B_1. Iron + Calcein W at pH 4.4. C and C_1. Cobalt + Calcein W at pH 4.4.

In curves A and B of Figs. 1, 2, and 3 the absorbance difference between about 600 and 700 mμ is due to the Cu–EDTA complex formed in the back-titration. This results in a small continuous increase of absorbance up to the equivalence point. This could be used for detection of the end-point graphically, but it is not desirable for automatic termination.

The automatic end-points are reproducible and accurate within 0.01 ml of 0.04 M copper solution, or better, so that relative errors are within about ±0.1%.

Apparatus

The Sargent-Malmstadt "Spectro-Electro" titrator was used[4]. A 5-ml buret, graduated in 0.01-ml divisions and equipped with delivery and refill stopcocks and titrant reservoir was used for the standard copper solution and a 10-ml self-zeroing buret equipped with delivery and refill stopcocks for the EDTA solution.

Reagents

Standard 0.04 M copper solution: Dissolve 2.542 g reagent grade copper sheet in slight excess of concentrated nitric acid, heat to boiling to expel oxides of nitrogen and dilute to the mark in a 1-liter volumetric flask with deionized water.

EDTA solution: To prepare a 0.04 M EDTA solution, dissolve 14.89 g of disodium ethylenediaminetetraacetate dihydrate in deionized water and dilute to 1 liter. Standardize this solution against the standard copper solution and store it in polyethylene bottles.

Buffer solution: Mix 638 ml of 2 N acetic acid with 362 ml of 2 N sodium acetate.

Calcein W indicator: 0.1% in 0.001 N sodium hydroxide.

PROCEDURE

Preparation of automatic titrator

The "Spectro-Electro" titrator is switched to the "Spectro" position; the polarity switch thrown to position 2; the filter wheel turned to the 500 mμ position; the pegs in the base set to properly position the 100-ml beaker; stirrer No. A, delivery tips and burets for standard EDTA reagent and copper titrant connected; and the titrant delivery set at about 3 ml/min.

Standardization of EDTA solution

Pipet a 4-ml aliquot of EDTA solution into a 100-ml beaker, dilute to about 45 ml with deionized water and add 10 ml of the buffer and 4 drops of the indicator solution. Insert beaker in titrator, push the start button to start the delivery of titrant and read the buret after automatic termination at the end-point.

Titration of copper

Dilute the slightly acid sample solution of copper to about 40 ml with deionized water in a 100-ml beaker, buffer strongly, add 4 drops of indicator solution and insert the beaker into the titrator. Start the stirrer and add EDTA solution until the appearance of the green fluorescence of the free indicator. Push the start button to start the delivery of copper titrant and read the buret after automatic termination at the end-point.

Titration of iron or cobalt

The same procedure as for the titration of copper is applied.

RESULTS AND DISCUSSION

Analysis of solutions containing relatively large amounts of copper, iron, and cobalt gave the results shown in Table I. It is seen that the relative errors are about ±0.1%

TABLE I

AUTOMATIC TITRATION RESULTS FOR SAMPLES CONTAINING KNOWN AMOUNTS OF COPPER, IRON, AND COBALT

Sample No.	*Copper*		*Sample No.*	*Iron*		*Sample No.*	*Cobalt*	
	Taken, mg	*Found, mg*		*Taken, mg*	*Found, mg*		*Taken, mg*	*Found, mg*
1	5.08	5.08	9	4.47	4.48	17	4.71	4.72
2	5.08	5.09	10	4.47	4.47	18	4.71	4.71
3	10.17	10.18	11	11.17	11.19	19	18.82	18.81
4	10.17	10.18	12	11.17	11.15	20	18.82	18.84
5	25.42	25.43	13	22.34	22.33	21	28.23	28.23
6	25.42	25.42	14	22.34	22.34	22	28.23	28.20
7	50.83	50.86	15	44.68	44.66	23	47.38	47.41
8	50.83	50.85	16	44.68	44.69	24	47.38	47.41

or less. When small amounts ($<$ 10 mg) of metals are determined, either a more dilute (0.01 M) EDTA solution or a 5-ml microburet, can be used in order to decrease the effect of buret reading errors; a 0.01 M standard copper solution is used as titrant.

At a delivery rate of 3 ml/min a blank of 0.03 ml of 0.04 M copper solution is applied; a blank of 0.05 ml is applied when 0.01 M copper solution is used as titrant. The excess of EDTA solution should be at least 1 ml so there will be enough time (at least 10 seconds) for the titrator to be activated before the end-point is reached. A large excess of EDTA solution increases the titration time unnecessarily.

ACKNOWLEDGEMENT

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SUMMARY

The metalfluorechromic indicator Calcein W is used as an absorption indicator at 500 mμ for the automatic titration of excess EDTA with copper titrant in the "Spectro-Electro" derivative titrator. Copper, iron or cobalt are determined by adding a small excess of standard EDTA, as visually indicated in the titrator by the fluorescence of Calcein W, with the subsequent automatic titration of excess EDTA. The intense colors of the EDTA complexes of these cations do not cause any difficulty by the automatic spectrophotometric method, and macro as well as micro quantities of the metals can be determined with relative errors of 0.1% or less.

RÉSUMÉ

Une méthode automatique de titrage spectrophotométrique est proposée pour le dosage du cobalt, du cuivre et du fer; on traite la solution à analyser par un excès d'EDTA que l'on titre au moyen d'une solution étalon de cuivre, en présence de calcéine W, comme indicateur.

ZUSAMMENFASSUNG

Es wird eine automatische spektrophotometrische Titrationsmethode zur Bestimmung von Kobalt, Kupfer und Eisen beschrieben. Die zu analysierende Lösung wird mit einem Überschuss von EDTA versetzt und mit Kupferlösung in Gegenwart von Calcein W automatisch zurücktitriert.

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Short Communications

Modification of Beckman DK-2 spectrophotometer circuitry and operation

The spectrophotometric determination or detection of ions having low molar absorptivities (such as the rare earths) can be enhanced on the Beckman DK-2 automatic recording spectrophotometer by modifying procedure and circuitry. Procedure A involves a modified nulling operation which will provide more than 1½ times the normal pen excursion on absorbance peaks without materially influencing the noise level. Procedure B involves a modification of the circuitry which, in combination with A, yields about 2½ times the normal pen excursion with a slight increase in the noise level. Relative graphs of erbium absorbance peaks are shown in Fig. 1.

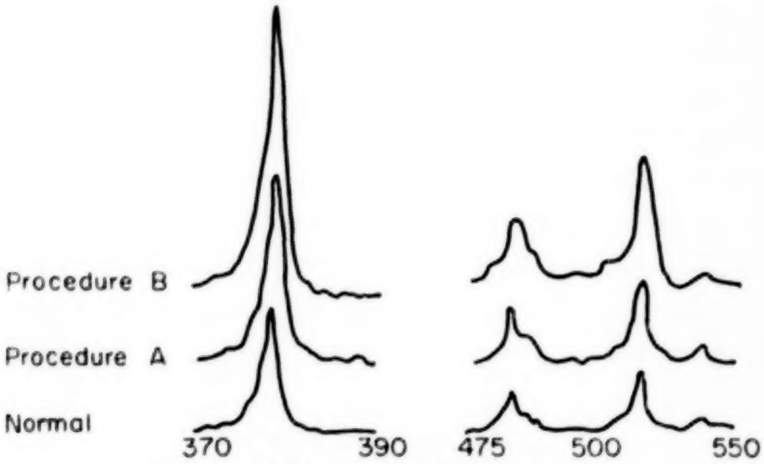

Fig. 1. Erbium absorbance peaks.

Procedure A

With the sample and reference solutions in place, zero the DK-2 in the normal manner. Then turn the zero adjust dial all the way to the left (applying maximum negative bias). Bring the needle back to the zero position with the 100 adjust dial. (For convenience in this operation, the −0.3 to +0.7 scale setting to locate the zero pen position can be used). These settings will now give greater pen excursion. For maximum resolution, a relatively slow speed with a short period should be used.

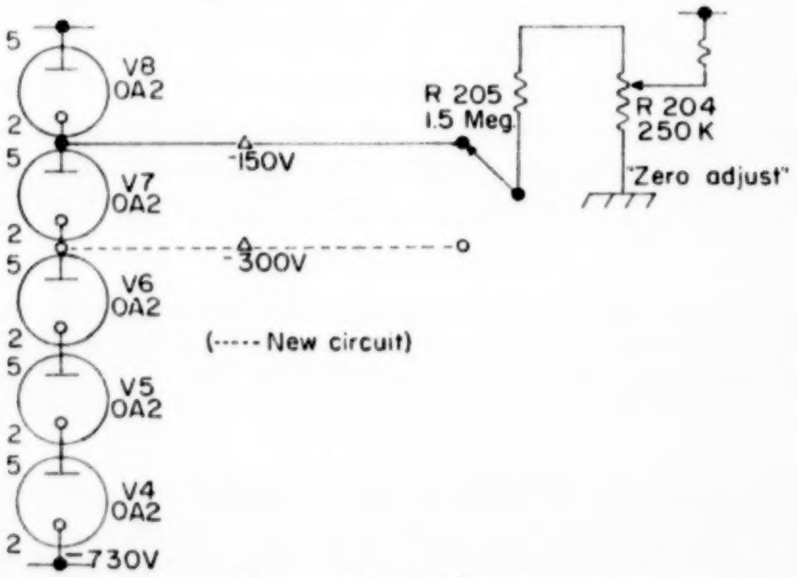

Fig. 2. Wiring diagram.

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Procedure B

When the amplifier is operated with increased gain, additional negative bias is required to set the recorder zero coincident with zero transmission. This additional voltage is obtained by changing connections at the photomultiplier voltage-supply regulator tubes so that minus 300 V is supplied to the bias control and series regulator rather then —150 V. For convenience, a switch is installed so the operator can change from one voltage to the other. With the switch in the —300 V position, the steps in procedure A are followed. A pen excursion of about 2½ times normal operation is obtained. The wiring diagram for the new circuit is shown in Fig. 2.

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Notes on the preparation and construction of silver reductor columns*

Silver for use in silver reductor columns is prepared by a number of methods. The reductor originally described by WALDEN, HAMMETT AND EDMONDS[5] used silver precipitated from an acidified silver nitrate solution by a copper sheet. Columns filled with this silver have a high reducing capacity but a very slow flow rate. The silver is very finely divided and packs down so tightly that liquid flow through the column is impeded; it is usually necessary to operate the column under reduced pressure. Silver prepared by reduction with sulfurous acid or formaldehyde is also finely divided and behaves similarly.

Silver deposited electrolytically as low density "trees" was introduced by SMITH AND CAGLE[4]. It is now commercially available and is in common use. Electro-deposited silver forms a porous column and permits a rapid flow rate. Its major disadvantage is that it requires frequent regeneration. Although this is simply performed by treatment with dilute ammonia it would be advantageous to have a column which did not require frequent regeneration.

A column combining the advantages of both types of silver and eliminating their disadvantages can be prepared by mixing the two types. By selection of various ratios of electro-deposited to copper-reduced silver, a column can be tailored to have various flow rates and capacities. For many applications a 1 : 1 ratio (v/v) is satisfactory. The use of pulverized silver metal (2) and metal platelets (1) should provide still greater flexibility in the preparation of a column.

In using a reductor column the operator must pay close attention to the height of the liquid and not allow the liquid to drain below the level of the silver. If air enters the column, entrapment ensues, and the solution may channel around much of the silver.

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* Publication authorized by the Director, U.S. Geological Survey.

The danger of air entrapment can be overcome by use of the column shown in Fig. 1. The design is similar to that of self-leveling ion-exchange columns[3]. With the delivery tube opening above the level of the top of the silver bed, the liquid level will always remain above the silver. A tall form funnel is used for the feed solution in order to take advantage of the increased hydrostatic head of the liquid. The flow rate can be controlled by adjustment of the stopcocks and the column can be used without attention by the operator.

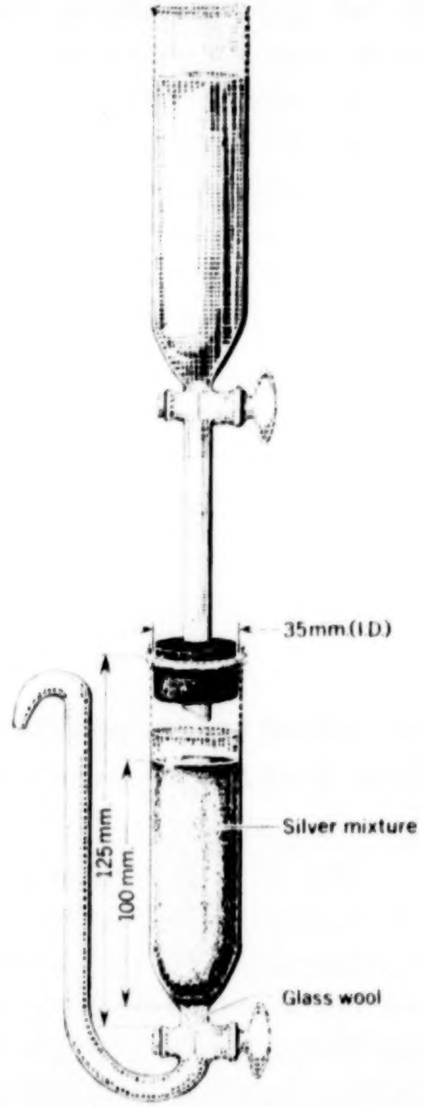

Fig. 1. Self-leveling reductor column.

The column used in this laboratory was constructed from two 125-ml cylindrical separatory funnels. To reduce breakage the exit tube was fabricated from polyethylene tubing. Commercially available self-leveling ion-exchange columns would be more convenient.

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Techniques of a. c. polarography

The purpose of this communication is to acquaint those contemplating the use of a.c. polarography with some phenomena observed by us which were not readily apparent. A Sargent Model XXI polarograph was modified according to Miller for use as an a.c. recording unit[1]. It was found to be necessary to ground the negative side of the recorder slidewire to obtain a referenced or non-floating a.c. response. This ground in no way interferes with the d.c. operation. Additional changes from the original work were the construction of the a.c. circuitry in an external unit (Fig. 1) and connecting the d.c. DME lead and the a.c. signal secondary connection at the series capacitor by means of an on-off switch. This allows the a.c. unit to be completely removed during d.c. operation. A master a.c.–d.c. switch was located on the polarograph panel. The 110-V a.c. for the transformer primary could not be placed on this switch since it resulted in a very high base line. It was necessary to place a 110-V a.c. on-off switch on the external unit. A 1,000 Ohm precision resistor was connected (on-off switch) across the cell leads in the a.c. unit so that calibration could be effected conveniently.

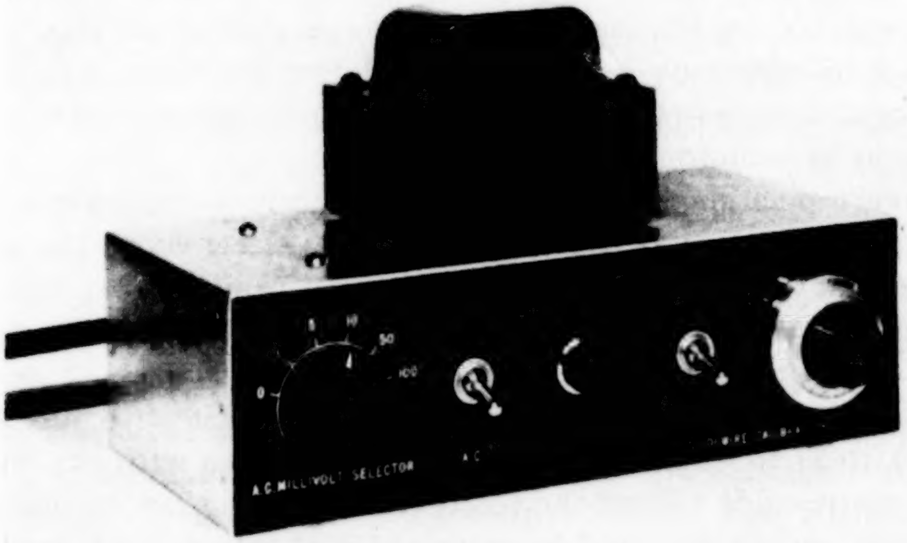

Fig. 1. a.c. control unit.

One advantage of a.c. polarography is the ability to obtain polarograms without first removing oxygen from the solution. On examination of Zn it was found that a large increase in peak height resulted if the solution was deaerated. Purging the cell with air caused the peak height to decrease. If the solution was made alkaline (pH 10) or if the solution was buffered (pH 6.5), a peak was obtained which was not sensitive to the presence of oxygen. The peak heights in alkaline media were much smaller, for identical concentrations, than those obtained in either deaerated unbuffered solutions or slightly acidic buffered solutions. The same effects were noted, differing only in magnitude, when Pb(II), Cd(II), Fe(II), Cr(III), and Ni(II) were examined. This sensitivity to oxygen was not seen with K, Ba, or BrO_3^-. These results can be explained by the interaction of hydroxyl, produced by the reduction of oxygen, with the former ions to form their insoluble hydroxides or hydrous oxides in the diffusion layer thus restricting the normal diffusion processes[2]. Hydroxyl ion does not form insoluble compounds with the latter ions. In buffered systems, hydroxyl is taken up and exerts no effect and in very alkaline solutions, the amount of hydroxyl generated is negligible compared to the concentration already present. BREYER, GUTMANN AND HACOBIAN[3] have reported these same effects for Zn, Pb(II), and Cd(II), offering a slightly different explanation for the Zn case based on the irreversibility of zincate ion reduction. However, we found basic zinc solutions were detected as well as Fe(II) and Ni(II), both of which, in the absence of complexing agents, are also irreversible reductions. RAMAIAH *et al.*[4], have also noted the decrease of Cd peak height with increasing pH.

Organic compounds whose reduction waves are due to proton reduction also exhibit a large increase in peak height if oxygen is removed. This was found to be true for gibberellic[5], malic, and oxalic acids. If the reduction is due to some other organic function, *e.g.*, aldehyde, double bond, nitro group, the effect of oxygen is not as pronounced. In unbuffered solutions, benzaldehyde and diethyl maleate waves show very slight decreases after removing oxygen. No change is observed if the solutions are buffered. Nitrobenzene and *p*-nitrophenol in unbuffered solutions exhibit slight increases of peak height after oxygen removal. These results may be caused by a pH effect in the diffusion layer (increasing in the presence of oxygen). Both benzaldehyde and diethyl maleate exhibit increased i_a/C ratios as pH increases in this region (pH 7)[6]. The i_a/C ratios of nitrobenzene and *p*-nitrophenol decrease when pH is increased[6]. No significant changes were observed in peak height for unbuffered solutions of iodoform or gibberellic acid (non-proton reduction peak).

Using a mercury pool anode, it was noted that accurate placement of the DME was important. The distance between the tip of the electrode to the mercury pool can vary considerably in d.c. polarography; however, using the a.c. system, a difference of 10 mm between runs would cause a peak height differential of 15%–20%.

Frequently, at low concentrations, sensitivity had to be increased, resulting in an increase in mercury drop oscillation signal. The most effective means found for damping was a 10 μf to 30 μf condenser inserted in series with the recorder input (terminal 4), negative side toward the recorder. This condenser decreased the signal 10% to 30% but sensitivity could be increased without as much oscillation being detected.

The author wishes to express his appreciation to Mr. HAROLD PLUMMER for the construction and wiring of the a.c. control unit.

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Über eine indirekte volumetrische Bestimmung von Anionen mit Redoxindikatoren

ERDEY UND BODOR[1] beschrieben die Verwendung von Variaminblauhydrochlorid (4-Amino-4′-methoxy-diphenylaminhydrochlorid) als neuen reversiblen Redoxindikator in der Massanalyse. In Lösungen mit reduzierenden Eigenschaften ist dieser Indikator farblos, in schwach oxydierend wirkenden dagegen entstehen blaue, violette oder rote Färbungen. Das Variaminblau fand breite Anwendung für Reaktionen, welche in schwach saurem Medium (pH = 2–6) verlaufen. In den vor Kurzem publizierten Arbeiten über argentometrische[2,3] und mercurimetrische[4,5] Bestimmungen der Chlorid-, Bromid-, Jodid-, Rhodanid-, Cyanid- und Salpetersäure-Ionen wurde auch dieser Indikator zur Anzeige des Titrationsendpunktes angewandt. Am Äquivalenzpunkt bei Fällungsreaktionen oder bei Reaktionen, in deren Verlauf schwach dissozierte Verbindungen entstehen, reagiert der Überschuss der Titrierlösung mit dem Indikator unter Blaufärbung der Lösung.

Variaminblau als Indikator wurde schon früher bei der volumetrischen Bestimmung von Zink und Blei mit Kaliumhexacyanoferrat(II)-lösung verwendet[6]. Die guten Ergebnisse, welche mit dieser Methode bei Bleibestimmungen erhalten wurden, veranlassten uns zur Ausarbeitung einer indirekten massanalytischen Bestimmungsmethode für Anionen, die mit Bleinitrat schwerlösliche Salze bilden. Wir fällten in essigsauren Lösungen, die mit Natriumacetat gepuffert waren, Sulfat-, Chromat- und Phosphat-Ionen mit überschüssiger 0.1 *N* Bleinitratlösung. Die Niederschläge wurden abfiltriert und mit 20%-igem Methanol–Wasser Gemisch ausgewaschen. Der Überschuss an Blei(II)-ionen wurde in Gegenwart von 1 Tropfen 0.1 *N* Kaliumhexacyanoferrat(III)-lösung und 3 Tropfen 1%-iger Variaminblauacetatlösung mit 0.1 *N* Kaliumhexacyanoferrat(II)-lösung titriert. Die Titrationen wurden bei etwa 60° durchgeführt. Am Äquivalenzpunkt verursacht der Kaliumhexacyanoferrat(II)-Überschuss einen Farbumschlag der Lösung von Violett nach milchgelb. Zwei- und dreiwertige Kationen stören und müssen vorher entfernt werden z.B. durch Fällung mit Natrium- oder Kaliumcarbonatlösung. Grosser Überschuss an Natrium-, Kalium- oder Ammonium-ionen stört ebenfalls. Die Ergebnisse sind gut reproduzierbar und stimmen mit den, nach anderen Verfahren erhaltenen Werten überein. Eine ausführliche Beschreibung der Methode wird demnächst erscheinen.

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BOOK REVIEWS

Separation and Identification of Food Colours Permitted by the Colouring Matters in Food Regulations, 1957, **The Association of Public Analysts, London, 1960, 31 p. Price: 21s. net.**

A committee appointed by the Association of Public Analysts has published its results on its investigation of the identification of 30 dyes which are permitted in Great Britain for use in foodstuffs. The results appear in a small book comprising 31 pages of which half are taken up with absorption curves. The methods for isolation and paper chromatographic separation of the dyes and their final identification by means of paper chromatography, absorption curves, and chemical tests, are described clearly and concisely. A dyestuff which does not belong to the list of those which are permitted is demonstrated by its failure to be identified as one of these. A continuation of these investigations is promised with the object of finding methods for the direct identification of dyestuffs which occur frequently and which are not in the list of those permitted by law.

F. REIMERS (Copenhagen)

Anal. Chim. Acta, 23 (1960) 300

Les cahiers techniques du Centre National de Coordination des Études et Recherches sur la Nutrition et l'Alimentation, IV. Le dosage microbiologique des vitamines du groupe B, Centre National de la Recherche Scientifique, Paris, 1959, 183 p.

Bien que l'analyse chimique soit en général plus sûre et plus rapide, elle ne permet pas encore de doser facilement toutes les vitamines du groupe B, surtout dans les milieux complexes. Dans ce cas, il faut avoir recours aux dosages microbiologiques qui présentent parfois l'avantage d'une grande sensibilité.

Dans un premier chapitre, l'auteur expose les principes des méthodes microbiologiques avec concision et clarté. Il en montre les difficultés, il met en évidence les sources d'erreurs. Il décrit les souches utilisées, les milieux de base des dosages, la technique en tube et sur gélose, la validité des résultats et des calculs, les méthodes d'extraction, la spécificité, problème si délicat et souvent difficile à résoudre et il termine cette première partie par un exposé fort bien venu sur les avantages et inconvénients des méthodes microbiologiques.

La suite de cet ouvrage comprend le dosage des vitamines du groupe B, soit: la thiamine, la riboflavine, les vitamines PP, B_6, l'acide pantothénique et le coenzyme A, la bioline, l'acide folique et la vitamine B_{12}. Chaque méthode y est décrite avec beaucoup de soins et de détails. Regrettons seulement que l'auteur n'ait pas donné à propos de chaque dosage, la sensibilité, la précision et l'exactitude.

Une bibliographie fort complète accompagne chaque chapitre de cet ouvrage.

D. MONNIER (Genève)

Anal. Chim. Acta, 23 (1960) 300

Trace Technique using the K 1000 Cathode Ray Polarograph, Vol. 1, par J. HETMAN, F.R.I.C., Southern Instruments, Camberley, Surrey, 1959, Prix 25s.

L'auteur a réuni, dans ce premier volume, diverses méthodes de dosage, effectuées au moyen du polarographe à rayons cathodiques K 1000. On y trouve, par exemple, le dosage du *m*-dinitrobenzène dans le benzène, du nitrobenzène dans l'aniline, le dosage simultané de l'acide fumarique et de l'acide maléique, le dosage simultané du cuivre, du plomb, du fer dans l'acide phosphorique, le dosage du fer dans le foie animal, etc. Trente méthodes sont ainsi proposées. Pour chacune d'elles, l'auteur indique en quelques mots le mode de préparation de l'échantillon, l'électrolyte de base utilisé, ainsi que l'électrode de référence. On trouve en outre une photographie du polarogramme, sur laquelle on peut relever les potentiels et estimer la sensibilité de la méthode. L'exposé se termine par l'interprétation des résultats et des remarques s'il y a lieu. Une bibliographie sur ces méthodes, dont l'auteur a fait une synthèse, termine ce volume.

Ouvrage intéressant, d'un emploi facile et qui permet d'un coup d'oeil de se rendre compte de la valeur d'une méthode et de ses possibilités.

D. MONNIER (Genève)

Anal. Chim. Acta, 23 (1960) 300

DETERMINATION OF HALOGENS IN POLYMERS AND OTHER PETROLEUM PRODUCTS BY A TWO-FURNACE COMBUSTION METHOD[*]

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(Received March 24th, 1960)

Analyses of organic materials for halogens and sulfur were carried out for many years by time-consuming wet chemical methods. During recent years there has been a trend toward combustion methods[1–5] because of their rapidity and versatility with regard to sample type and concentration.

A high temperature (2500°F) combustion method for determining chlorine and bromine was just recently presented by NICKSIC AND FARLEY[6]. A primary advantage of this method was stated to be the use of sodium bisulfite scrubbing solution. This solution permits rapid burning of relatively large samples with quantitative conversion of organic chloride and bromide to the ionic form for subsequent titration.

A method very similar to the one described in the preceding paragraph was used at this laboratory for analyzing chlorinated and brominated polymers, gas oils and residua having concentrations of chlorine and/or bromine up to 2%. In general, difficulty was encountered in burning samples larger than 0.2 g. In addition, small size samples resulted in small titrations. Thus, the importance of the blank and the random errors in the titration were magnified. It appeared that a method capable of burning larger samples would minimize these errors. With these facts in mind, the

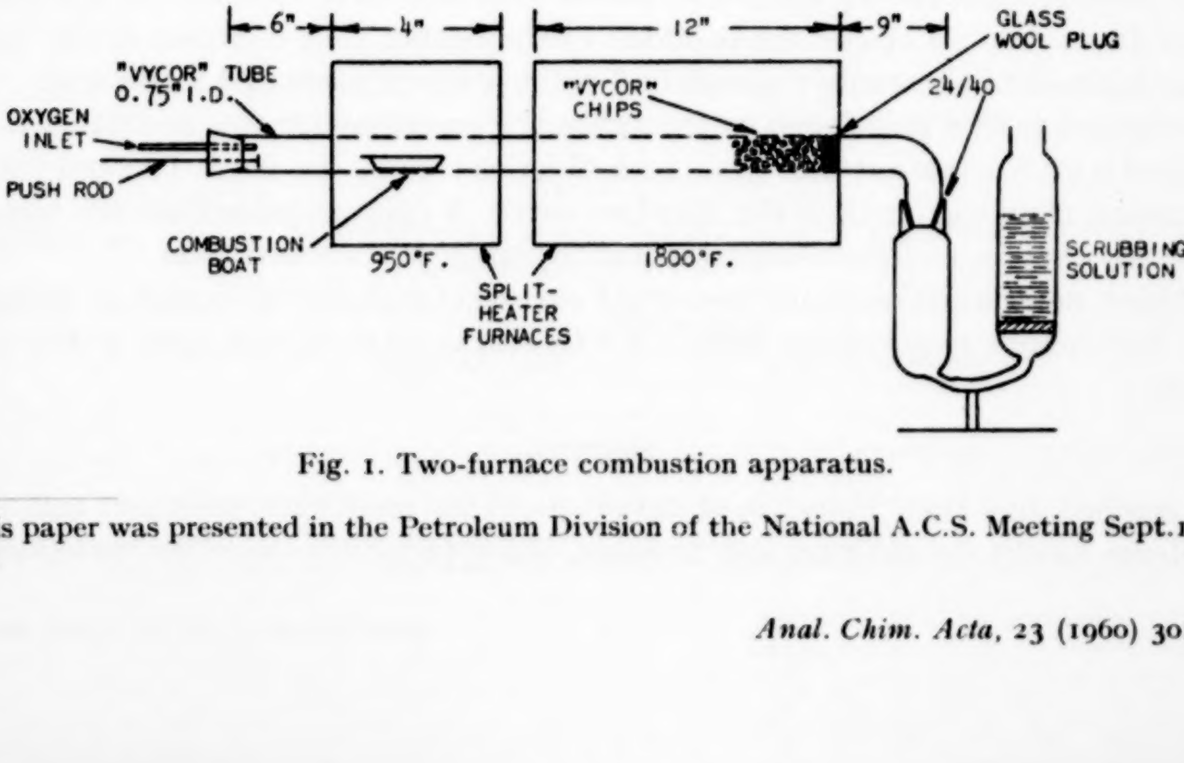

Fig. 1. Two-furnace combustion apparatus.

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[*] This paper was presented in the Petroleum Division of the National A.C.S. Meeting Sept. 12–17, 1958.

"Two-furnace" method described herein was developed. Its advantages over previously published high-temperature combustion methods are listed under "Discussion".

Apparatus and reagents

A schematic diagram of the apparatus is shown in Fig. 1. Both resistance furnaces are the hinged type. One is operated at about 950°F and the other at 1800°F ± 50°. The 950°F furnace can be adjusted to any desirable temperature for burning a particular type sample. For solid polymers and heavy oils, 950°F has been found satisfactory. The other furnace is maintained at 1800°F at all times during the analysis. The combustion tube is "Vycor" brand glass. This tube affords a clear view of the burning characteristics of the sample and also the exact position of the boat. The reagents required in this analysis are: (1) an aqueous scrubbing solution containing 2% sodium hydroxide and 0.5% hydrazine sulfate; (2) silver nitrate; (3) acetone; and (4) nitric acid.

PROCEDURE

In the analysis of solid polymers, it has been found that appreciable amounts of chloride may be picked up from the fingers of the analyst. For this reason it is important that the sample be handled only with forceps and it is further recommended that the exterior layer of the sample be removed and only the interior be used in the analysis. For other types of samples, routine precautions must be taken to insure that a representative sample is obtained.

The first furnace is brought up to a temperature suitable for burning the particular sample being analyzed and the second heater is brought up to a temperature of 1800°F. The oxygen rate is adjusted to 3 l/min. 100 ml of the scrubbing solution is poured into the absorber. The sample is weighed directly into a combustion boat. The amount of sample is governed by concentration of the halide, capacity of the boat, and volatility of the sample.

The boat is then inserted into the first part of the combustion tube and the stopper housing the oxygen inlet line and push rod is immediately inserted. The boat is pushed into the center of the first heater and is left there until the burning is apparently complete. About 5–10 min is required for this step. The boat is then pushed into the second furnace and allowed to remain there for an additional 10 min. Because of the high oxygen rate employed, the combustion products are completely swept from the combustion tube during this 15–20 min period.

The scrubbing solution is then transferred into a 400-ml beaker. The absorber is rinsed several times with small increments of distilled water and the rinsings added to the beaker. Each rinsing should be forced back and forth through the fritted disc several times. 100 ml of acetone is added to the beaker. The contents of the beaker are neutralized to the methyl orange end-point with concentrated nitric acid.

The beaker is then positioned on the automatic recording titrator and titrated with standard 0.01 *N* silver nitrate. Glass and silver electrodes are used. The end-point is determined from the break in the titration curve. A manual potentiometric titration can be used in place of the automatic but the latter saves much time.

A blank determination must be carried out exactly as above except no sample is used. The volume required for the blank titration is taken into account in the calculations.

RESULTS

This method has been found very satisfactory for analyzing polymers and other petroleum stocks for chlorine and bromine. Its applicability to other materials has not been studied except for the pure compounds listed in Table I. The analysis of iodine has not been examined.

TABLE I

HALOGEN CONTENT BY "TWO-FURNACE" METHOD

	Halogen, wt.%		*%*
	Theoretical	*Found*	*Recovery*
n-Butyl bromide	58.3	57.1	98
Hexachlorobenzene	74.8	75.6	101
Ferric ammonium chloride	65.8	63.8	96

The precision of the method with different analysts is approximately ±0.03% (2 *sigma*) at the 1% level as shown in Table II. Experience over a long period of time on a sample unknown to the analysts shows a precision of ±0.12% (2 *sigma*) at the 2% level. This is the precision that can be expected on routine samples in a control laboratory. The lower limit of the method is about 0.1% and is governed primarily by the size of sample employed. The upper range is unlimited.

The accuracy of the "Two-furnace" method compares closely with a high-temperature (2500°F) combustion method as shown in Table III.

TABLE II

PRECISION OF HALOGEN ANALYSES

Organic chloride sample *Chlorine, wt.%*	*Organic bromide sample* *Bromine, wt.%*
0.86	2.18
0.85	2.08
0.86	2.20
0.84	2.08
0.85	2.11
0.83	2.06
0.85	2.06
	2.03
	2.13
	1.95
	2.08
Average = 0.85	Average = 2.09
2 Sigma = ±0.03%	2 Sigma = ±0.12%

TABLE III

COMPARISON OF RESULTS BY HIGH-TEMPERATURE AND TWO-FURNACE COMBUSTION METHODS ON ORGANIC BROMIDE SAMPLE

Sample No.	*Bromine, wt.%*	
	High-temp. combustion	*Two-stage combustion*
1	2.02	1.99
2	2.18	2.17
3	2.41	2.37
4	2.02	2.00

DISCUSSION

The principal variables in the apparatus are temperature and oxygen rate. As stated before, the first furnace is regulated to a temperature which permits smooth burning of the particular type of sample being analyzed. The second furnace is maintained at 1800°F. The relatively high oxygen rate[7] of 3 l/min is required as shown in Table IV.

TABLE IV

EFFECT OF OXYGEN FLOW RATE ON RECOVERY OF CHLORINE

Flow rate, l/min	*% Recovery*
1.0	79
2.0	90
3.0	100

Several different aqueous scrubbing solutions have been investigated: (*1*) sodium carbonate, (*2*) sodium arsenite, and (*3*) sodium hydroxide–hydrazine sulfate. A 2% solution of sodium carbonate was found satisfactory for recovering chloride. No evidence of free chlorine or oxides of chlorine was found in the combustion products, so it was therefore deemed unnecessary to use a reducing agent for this purpose. However, this solution did not give complete recovery of bromine. Both the sodium arsenite and sodium hydroxide–hydrazine sulfate solutions were satisfactory for chlorine and bromine. The latter was chosen for routine work because of the toxic characteristic of arsenic compounds. With the sodium hydroxide–hydrazine sulfate solution, it was found that the addition of an equal amount of acetone improved the end-point by giving a sharper break in the titration curve.

The advantages of combustion methods over chemical methods, in general, are already known. The further advantages of the "Two-furnace" combustion method over other combustion methods are:

1. Volatile samples can be analysed. Liquids are contained in glass ampoules as used in conventional C and H analysis. The ampoule is charged into a cool part of the furnace tube and the sample burned by repositioning the first furnace to ignite gases issuing from the tip.
2. Improved control over pyrolysis of the sample permits the use of larger samples. This gives rise to a better titration figure and decreases the importance of the blank.
3. The analysis is rapid, 3 samples can be analyzed per hour on a single piece of equipment if an automatic titrator is employed.
4. The method is less subject to analyst error. A less experienced analyst can obtain satisfactory results.
5. Combustion is carried out at a lower temperature and, therefore, requires less expensive equipment.

SUMMARY

A rapid method for the determination of halides in organic liquids and solids has been developed. The procedure uses a two-stage furnace which allows rapid and controlled combustion of samples up to 20 g in weight. After combustion, the free halide is collected and determined in any conventional procedure.

RÉSUMÉ

Une méthode rapide est proposée pour le dosage des halogènes dans des substances organiques. Après combustion de la substance dans des quantités ne dépassant 20 g de poids, l'halogénure peut être titré électrométriquement par le nitrate d'argent.

ZUSAMMENFASSUNG

Beschreibung einer Schnell-methode zur Bestimmung von Halogen in organischen Substanzen mit kleinem Halogengehalt durch Verbrennung von bis zu 20 g Muster im Sauerstoffstrom und elektrometrische Titration mit Silbernitrat.

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THE DETERMINATION OF CHLOROFORM IN AQUEOUS SOLUTION

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Several methods which depend on assessment of the colour produced by such reagents as pyridine[1,2], resorcinol[3] or 2-naphthol[4] in the presence of alkalis have been proposed for the determination of chloroform in aqueous solution. The intensity of the colours produced depends on the conditions employed (*e.g.* temperature and alkali concentration) and the methods involve comparison with previously matched dye solutions or with a solution of chloroform of known strength treated at the same time under the same conditions.

Other methods are based on the determination of chloride ions liberated by alkaline hydrolysis of the chloroform. It has always been found necessary to use somewhat drastic conditions for this hydrolysis, *e.g.* KUNKE[5] concluded that pressure and heat are necessary for the complete hydrolysis of chloroform by alkalis and developed a procedure which involves heating the chloroform solution at 100° in pressure bottles with potassium hydroxide and methanol.

It has been stated that the carbylamine reaction goes to completion more readily than the alkaline hydrolysis of chloroform[6]. The disadvantages of this method include the unpleasant smell of the reaction products and a gravimetric determination of the chloride for which a considerable excess of silver nitrate is recommended (thirty times the theoretical quantity).

The present investigation[7] establishes the conditions under which chloroform is hydrolysed by alkalis at normal temperatures. In the proposed method, errors due to chloroform vapour being carried away with one of the reaction products, carbon monoxide, have been eliminated by selecting conditions which do not favour the evolution of this gas.

EXPERIMENTAL

All reagents used were AnalaR grade. Chloroform was purified immediately before use by the method of Fieser[8]. The hydrolyses were carried out in Pyrex glass stoppered reagent bottles. Chloride was titrated by Volhard's method.

Effect of size of the vapour space in closed reaction vessels

Owing to its volatility (saturated vapour pressure = 159 mm at 20°) chloroform initially present in aqueous solution will tend to pass into the space above the solution, thereby escaping hydrolysis. Depression of the solubility of chloroform in the presence of much alkali may accentuate this source of error (*e.g.* at 20° the solubility of chloroform per 100 ml is 0.98 g in water and 0.27 g in 4 *N* sodium hydroxide[9]). The results in Table I show the importance of keeping the vapour space in the reaction vessel as small as possible. This source of error must also be reduced to the minimum when preparing a 'standard' solution of chloroform.

It was also found that removing a solution of chloroform by means of a bulb pipette resulted in losses of up to 8% of the chloroform withdrawn; transference to the reaction vessel was therefore effected by fitting the flask containing the 'standard' solution of chloroform with a wash-bottle attachment and operating under pressure instead of suction.

TABLE I

INFLUENCE OF SIZE OF THE VAPOUR SPACE ON THE HYDROLYSIS OF CHLOROFORM BY AQUEOUS ALKALIS IN CLOSED VESSELS AT 20°

Alkali	*Vapour space* ml	*Reaction time* h	*Chloroform hydrolysed* %
4.8 *M* NaOH	4	4	80
4.8 *M* NaOH	4	18	79
4.8 *M* NaOH	24	4	69
4.8 *M* NaOH	120	4	42
4.8 *M* NaOH	192	4	34
4.8 *M* NaOH	360	4	30
4.5 *M* KOH	4	4	89
4.5 *M* KOH	4	18	88
4.5 *M* KOH	24	4	81
4.5 *M* KOH	120	4	59
4.5 *M* KOH	192	4	41
4.5 *M* KOH	360	4	31

Preparation of a solution of chloroform of known strength

Re-calibrate a 250-ml volumetric flask, containing a magnetic stirrer bar, to a new mark etched 1 cm below the stopper. Fill the flask to this mark with water and inject 0.5 ml of chloroform (from an Agla syringe) beneath the water surface and stopper immediately. Use magnetic stirring until the chloroform is completely dissolved. (Dissolution cannot be effected by shaking when the vapour space is so small).

Influence of alkali concentration

The results plotted in Fig. 1 show that potassium hydroxide (Curve A) is a more effective hydrolysing agent than sodium hydroxide (Curve B) at the same molar concentration. The presence ot ethyl alcohol appears to decrease the rate of hydrolysis (Curve C, potassium hydroxide in 50% aqueous alcohol).

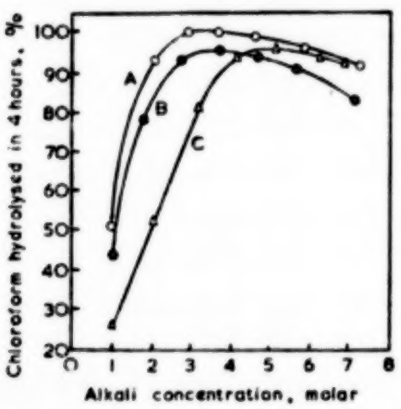

Fig. 1. Influence of the concentration of alkalis on the hydrolysis of chloroform at 20°.

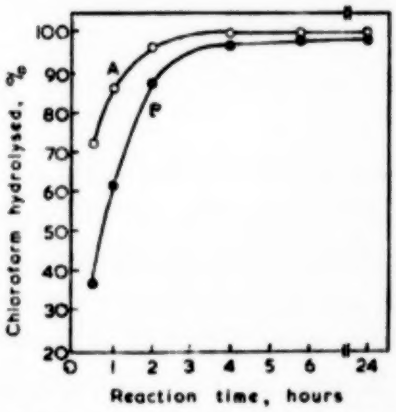

Fig. 2. Rate of hydrolysis of chloroform in 3.5 N aqueous alkalis at 20°.

Reaction time

In 3.5 M alkali at 20° the hydrolysis is virtually complete in about 6 h (Fig. 2) although the reaction is more rapid when potassium hydroxide (A) is used as compared with sodium hydroxide (B). It is most important that the reaction mixture is not disturbed during the hydrolysis because any agitation causes carbon monoxide to be evolved thus generating pressure and causing probable loss of chloroform vapour.

METHOD

Reagents

Potassium hydroxide 7 N; nitric acid 4 N; silver nitrate 0.1 N; potassium thiocyanate 0.1 N; ferric alum indicator, dissolve 14 g of ferric ammonium sulphate in 100 ml of water and add sufficient freshly boiled concentrated nitric acid to change the colour of the solution from reddish-brown to pale yellow. Use 2 ml for each titration.

Procedure

Pour sufficient 7 N potassium hydroxide into a 30-ml Pyrex reagent bottle to fill it to half its capacity and weigh. Transfer the chloroform solution, containing from 0.2 mg to 3 mg of chloroform per ml, into the alkali by using a wash-bottle attachment until the Pyrex bottle is nearly full (less than 1 ml of vapour space below the stopper), stopper immediately and weigh. During the transfer the wash-bottle jet should be kept below the surface of the alkali and raised just above the surface when adding the last few drops of chloroform solution. Mix the contents by inverting the bottle several times and allow it to stand for at least 6 h at 20° (or overnight at room temperature). Pour the solution into 25 ml of 4 *N* nitric acid, add one drop of phenolphthalein indicator solution, titrate with 4 *N* nitric acid until just colourless and then add 1 ml of 4 *N* nitric acid in excess. Add 20 ml of 0.1 *N* silver nitrate, filter off the silver chloride and titrate the excess of silver nitrate with potassium thiocyanate as in the usual Volhard procedure. The presence of phenolphthalein does not interfere with the determination of chloride.

RESULTS

Typical results obtained by this method are shown in Table II.

TABLE II

Chloroform added mg	*Chloroform found* mg	*Error* %
55.95	55.50	—0.8
51.45	51.15	—0.6
28.10	28.05	—0.2
22.05	21.90	—0.7
10.30	10.30[a]	less than 0.2
4.70	4.65[a]	—1

[a] 0.02 *N* solutions used for the chloride titrations.

In tests using aqueous solutions of carbon tetrachloride and of methylene chloride it was found that for each of these compounds less than 1% had reacted in 3.5 *N* potassium hydroxide at 20° during 24 h.

SUMMARY

The conditions under which chloroform in aqueous solution is completely hydrolysed by potassium hydroxide at room temperature have been established. The proposed method for the determination of chloroform involves hydrolysis followed by titration of the liberated chloride; the error is about 1%. Special precautions are necessary to avoid loss of chloroform vapour from the reaction mixture and during transference of chloroform solutions.

RÉSUMÉ

Une méthode est proposée pour le dosage du chloroforme. Elle consiste à effectuer une hydrolyse, au moyen d'hydroxyde de potassium, puis à titrer le chlorure libéré.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Chloroform durch Hydrolyse mit wässriger Kalilauge und Titration der gebildeten Chlor-Ionen.

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THE CHELOMETRIC DETERMINATION OF ALUMINUM, NICKEL AND MANGANESE WITHOUT PRIOR SEPARATION

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Although chelometric titrations are now being widely used for inorganic analysis, the majority of applications have been confined to the use of EDTA and NTA. Recently a few methods have been suggested using other complexans as reagents in order to improve the selectivity of the method[1-4].

The present paper deals with the use of hydroxyethylethylenediaminetriacetic acid (HEDTA) both as a reagent and as a masking agent. The pK (10.7) for the manganese–HEDTA complex is sufficiently low to suggest that at a pH of approximately 5 very little of the complex would be formed. The apparent stability constant for Mn at pH 5 is less than 5.5 and as such one would not expect Mn to interfere in titrations at this pH. The apparent stability constants (at pH 5) of nickel and copper are high enough (>8) so that a chelometric titration should be possible provided a suitable indicator were available.

In view of the color of the HEDTA complexes with nickel and copper, a fluorescent end-point appeared most appropriate. Preliminary titrations revealed that Calcein W and Calcein Blue gave rather sluggish end-points in the back-titration of an excess of HEDTA with a standard copper solution. It was apparent that the stability constants of copper with HEDTA and the indicators were not sufficiently far apart for a titration.

Two new indicators not previously described in the literature were available in which *n*-methylglycine had been substituted for iminodiacetic acid as the chelating substituent attached to the parent fluorescent indicator. The replacement of one of the carboxylic acid groups in Calcein W and Calcein Blue by the non-chelating methyl group would be expected to lower the stability constant of the copper-indicator complex. These indicators which are a condensation product of *n*-methylglycine, formaldehyde and fluorescein (and 4-methylumbelliferone) are named Methyl Calcein and Methyl Calcein Blue respectively. They are commercially available from the G. Frederick Smith Chemical Co., Columbus, Ohio. Either indicator gives a good end-point in the back-titration of an excess of HEDTA with a standard copper solution.

Since the stability constant for the aluminum–HEDTA complex has not been reported, a preliminary investigation of the feasibility of using HEDTA as a reagent for aluminum was initiated. An aluminum solution was prepared and standardized using an excess of EDTA and a back-titration with a standard copper solution. The standardization of the aluminum solution was then repeated, but HEDTA was substituted for EDTA as the reagent. The values obtained with both reagents were indistinguishable. The nickel solution was standardized in a similar manner.

The titration of the sum of the nickel and aluminum proceeded differently with HEDTA than with EDTA. If the back-titration with copper is done with the hot solution a fading end-point results. The aluminum–HEDTA complex apparently is involved in a displacement reaction which results in the formation of a copper–HEDTA complex. This difficulty is eliminated if the solution to be titrated is cooled to room temperature prior to the back-titration. The kinetics of the reaction at room temperature are such that the displacement is insignificant during the titration.

The manganese determination is made on the same solution by means of a direct titration with EDTA at a pH of approximately 9.5. The HEDTA used in the first back-titration serves to mask the nickel and copper present in the sample. Aluminum forms a complex with fluoride and is partially precipitated. The precipitate does not interfere with the manganese titration.

PROCEDURE

To a solution containing aluminum, nickel and manganese add an excess of HEDTA over that which is required to react with aluminum and nickel present. Adjust the pH to approximately 5 and add 10 ml of a sodium acetate–acetic acid buffer (1 *M* each) and bring to a boil. Cool to room temperature, add three drops of a 0.1% aqueous solution of Methyl Calcein or Methyl Calcein Blue and back-titrate with a standard copper solution to determine the sum of the aluminum and nickel. The end-point is characterized by the quenching of the fluorescence of the free indicator. Add 0.5 g of ammonium fluoride, heat the solution to its boiling point then back-titrate the HEDTA released from the aluminum complex with a standard copper solution. Add 1 g of potassium tartrate, adjust the pH to 9.5 with sodium hydroxide solution and titrate the manganese with EDTA solution. This end-point is characterized by the appearance of the fluorescence of the free indicator. Representative data for these titrations are shown in Table I.

TABLE I

REPRESENTATIVE DATA FOR THE TITRATIONS OF Al, Ni AND Mn WITHOUT PRIOR SEPARATIONS

mg Ni		*mg Al*		*mg Mn*	
Present	*Found*	*Present*	*Found*	*Present*	*Found*
9.96	9.94	10.04	9.97	9.86	9.93
9.96	9.94	10.04	9.97	9.86	9.87
9.96	9.93	10.04	9.95	9.86	9.90
9.96	9.93	10.04	9.98	9.86	9.85
9.96	9.94	10.04	9.97	9.86	9.82

DISCUSSION

The titration of aluminum and nickel in the presence of manganese is dependent upon several favorable equilibria. Manganese must form a weak enough complex with HEDTA so that is is not partially titrated during the back-titration. In addition manganese must quench the fluorescence of the indicator at a pH of 9.5 but must not quench the fluorescence at 4.8.

It was apparent that HEDTA forms a complex with aluminum much faster than EDTA. In fact, with only aluminum present in a solution, it was not usually necessary to heat the solution. Occasionally, however, a low result for aluminum was obtained and this was attributed to incomplete formation of the complex prior to the back-titration. For this reason it is preferable to heat the solution in order to ensure complete formation of the aluminum-HEDTA complex. The back-titration of the hot solution resulted in an incomplete displacement reaction wherein the copper displaced aluminum from its HEDTA complex. If the solution was cooled back to room temperature, this displacement was not significant. The displacement of aluminum from its complex with HEDTA by fluoride ion was best accomplished in a hot solution. The subsequent titration of the HEDTA released from the aluminum and the direct manganese titration with EDTA may be conducted in either hot or cold solutions. During the manganese titration at a pH of 9.5 the nickel and copper are masked by HEDTA. The aluminum undoubtedly exists in several forms, however, none of these interfere in the titration. The addition of tartrate serves to hold the manganese in solution during the titration.

SUMMARY

Hydroxyethylethylenediaminetriacetic acid is used as a selective reagent for the chelometric determination of Al and Ni in the presence of Mn. Mn is subsequently determined in the same solution by means of a direct EDTA titration. The reagent for the first titrations serves as a masking agent during the manganese determination. Methyl Calcein or Methyl Calcein Blue serves as a metalfluorechromic indicator for the determinations.

RÉSUMÉ

Une méthode est proposée pour le dosage de l'aluminium et du nickel, en présence de manganèse par titrage au moyen de l'acide hydroxyéthyléthylènediaminotriacétique. Le manganèse est ensuite dosé dans la même solution par EDTA.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur komplexometrischen Bestimmung von Aluminium und Nickel sowie Mangan in der gleichen Lösung. Aluminium und Nickel werden mit Hydroxyäthyl-äthylendiaminotriessigsäure und anschliessend das Mangan mit EDTA titriert.

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DETERMINATION OF AROMATIC PRIMARY AMINES AND COMPOUNDS CONTAINING REACTIVE METHYLENE GROUPS BY DIAZOTISATION AND C-NITROSATION REACTION USING ALKYL NITRITES

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The Griess reaction of aromatic primary amines with nitrous acid in presence of a mineral acid[1] can be represented by the following general equation:

$$(ArNH_3)X + HNO_2 = (ArN_2)X + 2H_2O$$

In many cases the reaction proceeds quantitatively and with sufficient velocity to permit direct titration of the amines. It has long been used for the determination of the aromatic primary amines, especially in the dye industry, but the first critical examination of the diazotisation reaction for quantitative purposes was done by PHILLIPS AND LOWY[2]. The method has been employed for determining *p*-phenylenediamine[3]; starch–iodide paper was used as external indicator. The main disadvantages of the method are:

(*1*) The slow rate of diazotisation of certain amines (amines substituted with electronegative groups).

(*2*) Decomposition of nitrous acid during the reaction and volatilisation of the decomposition products.

(*3*) The use of an external indicator.

In order to overcome the last difficulty, potentiometric titrations were used by MULLER[4], SINGH[5,6] and SAXENA[7]. However, nitrous acid was still lost. Alkyl nitrites have therefore been examined to see if they could replace alkali nitrites. The alkyl (butyl and ethyl) nitrites proved to have distinct advantages over sodium nitrite for the titration of the amines with potentiometric end-point detection. It is surprising that the Knoevenagel method[8,9] of diazotisation which is so frequently used in preparative organic chemistry has not previously been tested for the determination of amines.

It has also been found that certain other compounds react quantitatively with nitrous acid (*e.g.* compounds containing reactive methylene groups and secondary amines) and can be determined by the method of C-nitrosation using alkyl nitrites. From a survey of the C-nitrosation reaction[10,11] there appear to be a large number of compounds which react with alkyl nitrites quantitatively to give C-nitroso compounds. The reaction proceeds smoothly at room temperature and the rate of consumption of nitrous acid is almost the same as the rate of hydrolysis of alkyl nitrite, so that losses due to decomposition are avoided.

EXPERIMENTAL

Preparation and standardisation of alkyl nitrite solutions

Ethyl nitrite and butyl nitrite were prepared by the method described in "Organic Syntheses"[12]. Gaseous ethyl nitrite was directly absorbed in absolute ethanol while butyl nitrite was purified by distillation under reduced pressure (24°, 43 mm). An approximately 0.2 *M* solution of butyl nitrite was prepared by dissolving 20.6 g of butyl nitrite in 1 l of absolute ethanol. The ethanol used for the preparation of these solutions was purified by distilling over potassium hydroxide.

The gasometric method is recommended for the assay of alkyl nitrites in the British Pharmacopeia[13]; but in the present work standardisation by titration against $KMnO_4$ and by potentiometric titration against sulfanilic acid were preferred, so that the conditions for the standardisation were similar to those used in the actual determinations. The results of standardisation by both these methods were identical.

Stability of alkyl nitrite solution

In aqueous solution alkyl nitrites are hydrolysed even at very low hydrogen ion concentration[14] hence the ethanol used should be distilled over potassium hydroxide. In presence of excess of alcohol the equilibrium of the reaction

$$ROH + HNO_2 \rightleftarrows RONO + H_2O$$

is shifted towards the left. It was found that if amber coloured bottles were used, the solution was quite stable for over 10 days and the change in the titre amounted to less than 0.05 ml for 20 ml on standing for one week. The decomposition of the alkyl nitrites is inhibited by adding glycerol[15] and therefore a few drops of glycerol were always added to the stock solution. There is always a possibility of volatilisation of some alcohol from the standard solution and therefore the solution was stored in well-stoppered bottles and the bottles were immediately stoppered after use. It is also recommended that the open end of the burette should be closed by inverting a test-tube over it.

Determination of aromatic primary amines by diazotisation with alkyl nitrites

The amines chosen for determination by the potentiometric method using the diazotisation reaction with alkyl nitrites were (*1*) aniline (b.p. 183°), (*2*) α-naphthylamine (m.p. 50.5°), (*3*) *p*-toluidine (m.p. 44.5°), (*4*) *p*-nitroaniline (m.p. 147°), (*5*) *o*-nitroaniline (m.p. 70.5°), (*6*) *m*-nitroaniline (m.p. 114°), (*7*) benzidine (m.p. 127°), (*8*) *p*-chloroaniline (m.p. 70.5°), (*9*) *p*-phenylenediamine (m.p. 140°), (*10*) *o*-aminobenzoic acid (m.p. 144°), and (*11*) *m*-phenylenediamine hydrochloride.

The samples of the amines used were of A.R., B.D.H. or C.P. quality and in case of doubtful purity they were standardised by the acylation method[16]. Approximately 0.05 *M* solutions of the amines were prepared by dissolving weighed amounts of the amines in HCl–alcohol–water mixtures.

Procedure

10 ml of the amine solution was pipetted into the titration vessel and 5 ml of concentrated hydrochloric acid was added. The electrode system consisted of a bright platinum spiral as indicator electrode and a saturated calomel reference electrode.

The e.m.f. of the cell was measured both with the help of a PYE potentiometer and Cambridge pH meter (Bench type). The titration was started by adding the alkyl nitrite solution from a micro burette the tip of which dipped into the amine hydrochloride solution. The solution was stirred magnetically and the temperature of the titration vessel was kept at 5° ± 0.5 by surrounding with cold water. During the titration the potential increased fairly steadily; at the end-point a sudden increase in the e.m.f. of the order of 80 to 130 mV was observed. After this the potential remained more or less constant. The potential difference was read 2 min after the addition of alkyl nitrite *i.e.* when the potential became steady. As a typical example the readings of the titration of aniline and alkyl nitrites are given in Table I.

TABLE I

No.	*Butyl nitrite added ml*	*e.m.f. mV*	*E*	*No.*	*Ethyl nitrite added ml*	*e.m.f. mV*	*E*
1	0.0	380	—	1	0.0	332	—
2	0.1	470	90	2	0.1	448	116
3	0.5	500	30	3	0.5	460	12
4	1.0	538	38	4	0.8	468	8
5	1.5	576	38	5	1.0	474	6
6	2.0	616	40	6	1.2	480	6
7	2.1	622	6	7	1.4	484	4
8	2.2	629	7	8	1.6	290	6
9	2.3	636	7	9	1.8	496	6
10	2.4	643	7	10	2.0	506	10
11	2.42	644	1	11	2.1	510	4
12	2.44	646	2	12	2.2	514	4
13	2.46	650	4	13	2.3	518	4
14	2.48	743	93(Max)	14	2.4	524	6
15	2.50	746	3	15	2.42	526	2
16	2.52	747	1	16	2.44	528	2
17	2.56	749	2	17	2.46	534	6
18	2.60	750	1	18	2.48	654	120(Max)
19	2.7	751	1	19	2.50	658	4
20	2.8	751	0	20	2.52	660	2
21	3.0	751	0	21	2.54	662	2
22	3.5	750	−1	22	2.56	664	2
23	4.0	749	−1	23	2.60	666	2

The graphs of e.m.f. *vs.* the volume of alkyl nitrite added for different amines are given in Figs. 1, 2 and 3. It can be seen that most of these aromatic primary amines can be titrated satisfactorily with alkyl nitrite solution using potentiometric end-point detection.

Determination of compounds containing reactive methylene group

The compounds chosen for C-nitrosation were, (*1*) acetyl acetone (b.p. 139°), (*2*) dimedone (m.p. 149°). It has been reported that the nitrosation reaction with these compounds is almost quantitative[17]. The solutions of these compounds were prepared

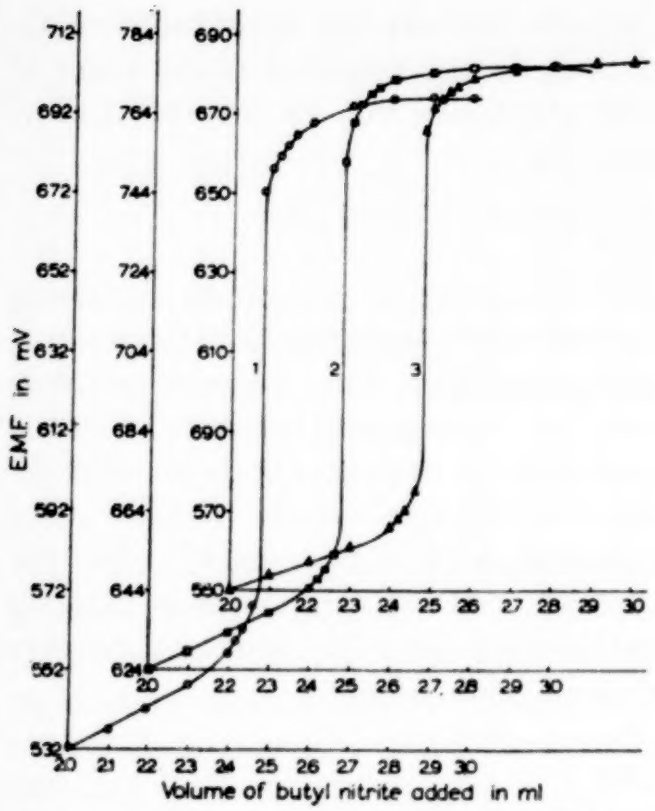

Fig. 1. E.m.f. *versus* volume of alkyl nitrite added for (*1*) *p*-phenylenediamine, (*2*) benzidine, (*3*) *m*-phenylenediamine hydrochloride.

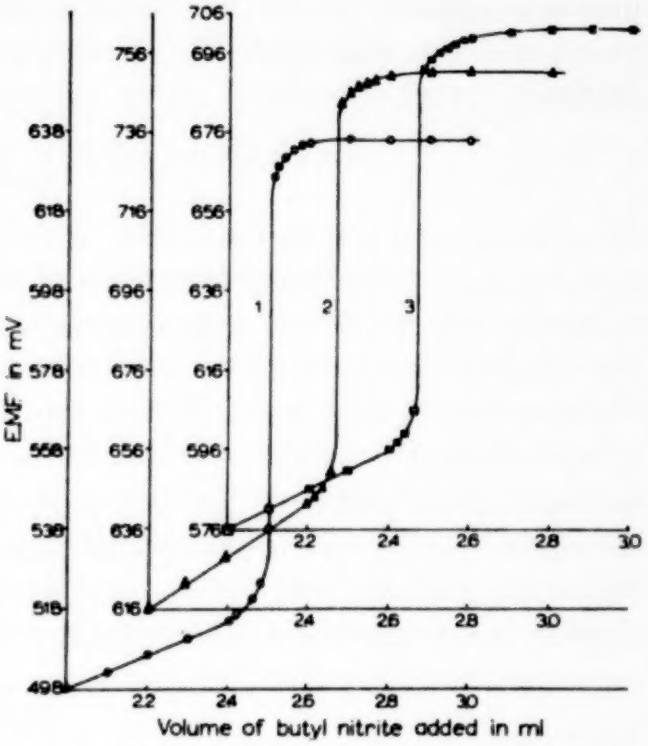

Fig. 2. E.m.f. *versus* volume of alkyl nitrite added for (*1*) α-naphthylamine, (*2*) aniline, (*3*) *p*-toluidine.

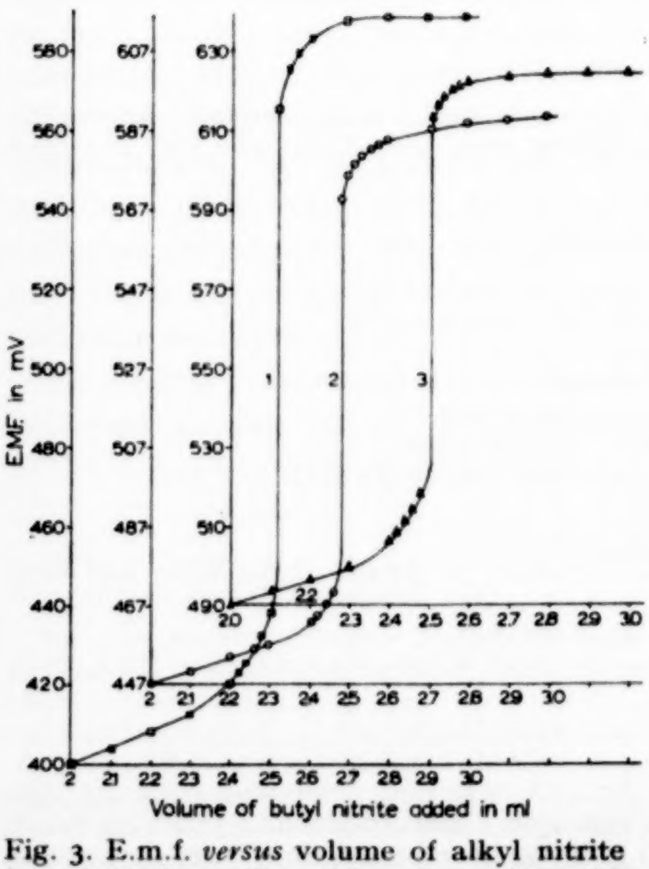

Fig. 3. E.m.f. *versus* volume of alkyl nitrite for (*1*) *m*-nitroaniline, (*2*) *o*-nitroaniline, (*3*) *p*-nitroaniline.

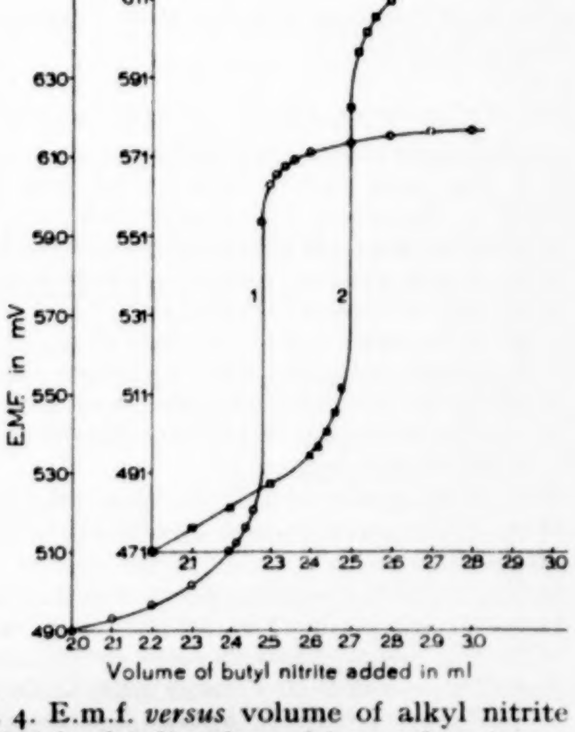

Fig. 4. E.m.f. *versus* volume of alkyl nitrite added for (*1*) dimedone, (*2*) acetyl acetone.

in alcohol and the titrations were performed exactly as described above for aromatic primary amines. At the end-point a sudden jump in the potential of the order of 70–75 mV was observed. Fig. 4 represents the graph of e.m.f. *vs.* volume of alkyl nitrite.

DISCUSSION

Diazotisation of primary aromatic amines and C-nitrosation of compounds containing reactive methylene group by means of alkyl nitrite can be used for the determination of these compounds with potentiometric end-point detection. The temperature during the reaction should be maintained between 5 and 10°. Nitrous acid is generated during the reaction at such a rate that it can be consumed by reactants without prior decomposition. Hence the method has a distinct advantage over the method using sodium nitrite solution as the source of nitrous acid. Potentiometric determination of the end-point has an advantage over starch–iodide paper used as an external indicator. The method should be equally satisfactory for other aromatic primary amines and compounds containing a reactive methylene group.

SUMMARY

A titrimetric method for the determination of primary aromatic amines and compounds containing a reactive methylene group by diazotisation and C-nitrosation respectively is described. The end-point is detected potentiometrically with a platinum indicator electrode. The advantages of standard alkyl nitrite solutions over alkali metal nitrites is discussed.

RÉSUMÉ

Une méthode est décrite pour le dosage volumétrique des amines aromatiques primaires et des composés renfermant des groupements méthyléniques (acétylacétone, dimédon), par titrage au moyen de nitrite d'alcoyle. Le point final est déterminé potentiométriquement.

ZUSAMMENFASSUNG

Beschreibung einer volumetrischen Methode zur Bestimmung primärer aromatischer Amine und aktiver Methylengruppen durch Titration mit Alkylnitritlösung. Der Endpunkt wird potentiometrisch bestimmt.

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DIE QUANTITATIVE BESTIMMUNG VON SULFONAMIDEN MITTELS IONENAUSTAUSCHERPAPIER

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Die qualitative wie auch die quantitative Analyse von Sulfonamiden ist zufolge der grossen Bedeutung dieser Verbindungen stark ausgebaut worden. Dies bedeutet jedoch nicht, dass neue, in mancher Hinsicht bequemere Bestimmungsmethoden nicht auffindbar sind. Dieser Aufsatz soll die Aufmerksamkeit auf eine neue, quantitative Bestimmungsmethode dieser Substanzen lenken, nämlich auf Bestimmungen mittels Ionenaustauscherpapier.

Ionenaustauscherpapier, welches seit 1954 bekannt ist[1], besteht aus Zellulosefasern zwischen welchen beliebige Ionenaustauscher eigebettet sind[2]. Es ist also weder mit Ionenaustauscherpapier aus chemisch veränderten Zellulosefasern[3-5], noch mit Ionenaustauschermembranen[6] zu verwechseln. Da die Anteile der Ionenaustauscher in der Zellulosemasse weitgehend gleichmässig verteilt sind und in den gegebenen Umständen die Ionenaustauscher im Gegenstrom mit Elektrolyten praktisch stöchiometrisch reagieren, eignet sich Ionenaustauscherpapier ausgezeichnet zu quantitativen Bestimmungen. Durch einfaches Einsaugen bestimmter Volumen von Elektrolytlösungen entstehen auf dem Papier Zonen, deren Flächen den Mengen der Elektrolyte direkt proportional sind. Dieses Verfahren ist an erster Stelle zu Bestimmungen einzelner Verbindungen, wie auch zur summarischen Bestimmung ähnlicher Substanzen verwendbar, obwohl in verschiedenen Fällen auch Komponenten aus Gemischen, gruppenweise oder einzeln, gleichzeitig bestimmt werden können. Naturgemäss werden mit diesem Papier kleine Substanzmengen, im Bereich von Milligrammen und Mikrogrammen bestimmt.

Zu solchen Substanzen welche mit Hilfe von Ionenaustauscherpapier quantitativ bestimmt werden können, gehören auch Sulfonamide. An etlichen Beispielen wird weiter der Analysengang erläutert.

METHODIK

Reagenzien und Hilfsmittel

Kationenaustauscherpapier. Austauscherpapier mit verschiedenem (1–10%) Gehalt an Kationenaustauscher wurde verwendet. Es wurde in Streifen von 10 mm Breite und — je nach Bedarf — 70–150 mm Länge geschnitten. Das Austauscherpapier wie auch die dazu verwendeten Kationenaustauscher wurden in unserem Institute hergestellt. Die in Fig. 1 und Fig. 2 dargestellten Ergebnisse wurden bei Verwendung eines phenol-sulfonsauren Kationenaustauschers (in der H-Form) erhalten. *Sulfonamide.* Für die Untersuchungen wurden 0.02%-ige wässerige Lösungen verwendet. Prontosil rubrum und Sulfanilguanidin wurden in Aceton gelöst und mit Wasser verdünnt. *Ehrlichs Reagenz.* Es wurde 0.5 g Reagenz (*p*-Dimethylaminbenzaldehyd) in 5 ml 2 *N* HCl gelöst und mit Wasser auf 250 ml aufgefüllt. *Tüpfelplatte mit gleich grossen Vertiefungen.* Es wurden Platten mit Vertiefungen von 1 ml Rauminhalt verwendet. *Mikropipette. Aufhängevorrichtung*

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für die Streifen von Austauscherpapier. Für wässerige Lösungen zweckmässig ein Gestell aus Kunststoff. *Grosser Glasbehälter*. Er dient als chromatographische Kammer. *Durchsichtiges Millimeterpapier*.

Ausführung der Bestimmungen

In fünf Vertiefungen der Tüpfelplatte werden mit Hilfe einer Mikropipette steigende Volumen der Standardlösung eingetragen. In drei andere Vertiefungen kommen gleiche Volumen der zu analysierenden Lösung. Danach werden alle eingetragenen Lösungen mit Wasser auf das gleiche (z.B. 1.0 ml) Volumen gebracht. Im Falle von Prontosil rubrum wird zweckmässig 0.1 *N* Ammoniak anstatt Wasser zur Verdünnung der Proben angewendet.

In Abständen, die den Vertiefungen der Tüpfelplatte entsprechen, werden nun Streifen des Austauscherpapiers zwischen zwei, mit Gummiringen aneinander gepresste Glasstäbe geklemmt. Die eingeklemmten und entsprechend beschrifteten Enden der Streifen ragen etwas über die Glasstäbe hinaus. Die anderen Enden werden mittels kleinen Glasklammern mit schmalen Streifen (2–3 mm breit und 20 mm lang) gewöhnlichen, reinsten Filtrierpapiers verbunden. Diese schmalen Dochte verringern die Geschwindigkeit des Aufsaugens der Lösungen. Sie verhindern auch das Eintreten eines statischen Gleichgewichtes mit der Lösung in dem Teile des Austauscherpapiers, welcher unmittelbar in die Lösung eingetaucht wäre. Bei Verzicht auf möglichst grosse Genauigkeit der Bestimmungen können diese Papierdochte weggelassen werden.

Die so vorbereiteten Streifen werden auf niedrigen Stativen über die Tüpfelplatte gehängt und die Enden der Dochte in die entsprechende Vertiefungen getaucht. In einer anderen Anordnung können die Lösungen auch in horizontaler Richtung auf das Ionenaustauscherpapier geleitet werden[7]. Die oberen, zwischen den Glasstäben herausragenden Enden der Streifen werden mit einer Lage Lignin bedeckt, welches das durchfliessende Wasser aufsaugt. Die so montierte Vorrichtung wird mit einem Glasbehälter bedeckt. Bei Bestimmungen von Prontosil rubrum oder Sulfanilguanidin wird unter den Behälter eine Schale mit Aceton und Wasser (3 : 2) gestellt.

Nachdem alle Lösungen durch die Streifen aufgesaugt wurden, werden die Dochte entfernt und die durch Sulfonamide besetzten Zonen sichtbar gemacht. Zu diesem Zwecke werden die Streifen mit Ehrlichs Reagenz besprüht. Es erscheinen scharf begrenzte, orangefarbene Zonen. Diese können auch als Diazofarbstoffe sichtbar gemacht werden. Die Zonen von Prontosil rubrum sind von selbst farbig. Die Streifen werden nun getrocknet und die Flächen der Zonen mit Hilfe von durchsichtigem Millimeterpapier ermittelt. Die zahlenmässigen Werte für die Sulfonamidmenge und die entsprechenden Zonenflächen der Standardlösungen werden in ein Koordinatensystem eingetragen und die Schnittpunkte mit einer Geraden verbunden. An Hand dieser Standardlinie wird die zu ermittelnde, unbekannte Menge des Sulfonamides graphisch gefunden.

RESULTATE UND DISKUSSION

Es wurden viele Bestimmungen mit gutem Erfolg durchgeführt. Eine dieser Bestimmungsreihen ist für die erwähnten Sulfonamide auf Fig. 1 angeführt. Jede Reihe umfasst vier Konzentrationen desselben Sulfonamides. Wie ersichtlich, besteht eine direkte Abhängigkeit zwischen Zonenfläche und Sulfonamidmenge. Die Bestimmungen wurden auf Papier mit ähnlichem, jedoch nicht identischem Gehalt an Austauscher durchgeführt. Eine Ausnahme ist die Bestimmung von kleinsten Mengen von Sulfanilacetamid, wozu „verdünntes" Austauscherpapier verwendet wurde. Eine dieser Bestimmungsreihen ist auf Kurve 8 in Fig. 1 gestrichelt dargestellt. Die vier Konzentrationen entsprechen in diesem Falle 4, 8, 12, 16 µg pro 1.0 ml. Um den Bestimmungsfehler möglichst klein zu halten, wurden für die Analysen die minimalen Substanzmengen gebraucht, die Zonenflächen von mindestens 40 mm² ergaben. Die Flächen können mit einer Genauigkeit von 1–2 mm² bestimmt werden. Die Differenz zwischen den zugegebenen und gefundenen µg Mengen der Sulfonamide liegt in den Grenzen von ± 3%.

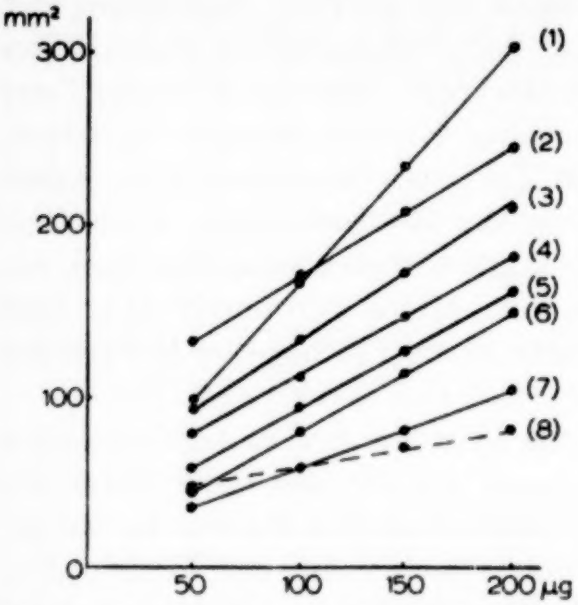

Fig. 1. Die lineare Abhängigkeit der Zonenfläche von der Substanzmenge. 1, Sulfanilamid; 2, Sulfanilharnstoff; 3, Sulfanilacetamid; 4, Sulfanilamid + Marfanil; 5, Sulfanilguanidin; 6, Prontosil rubrum; 7, Sulfanilamidothiazol; 8, Sulfanilacetamid (4, 8, 12, 16 µg).

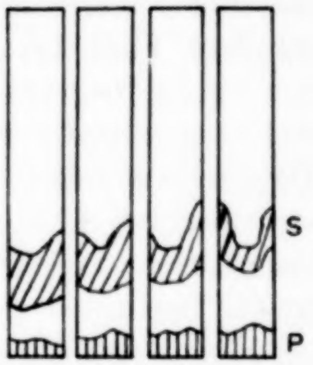

Fig. 2. Trennung von Sulfanilamid (S) und Prontosil rubrum (P).

Wie schon am Anfang erwähnt, können auch Gemenge von Sulfonamiden (z.B. Mephaderm, Kurve 4 in Fig. 1) wie auch Komponenten von Gemischen auf einem Streifen gleichzeitig bestimmt werden. Als Beispiel der Bestimmung von Komponenten möge die Analyse eines Gemisches von Sulfanilamid und Prontosil rubrum dienen. Es wurden Gemische mit abnehmendem Sulfanilamid Gehalt und gleichzeitig steigendem Gehalt an Prontosil rubrum hergestellt. Die acetonhaltige Lösung dieser Substanzen wurde mit 0.25 N Ammoniak (15% des Gesamtvolumens) versetzt und in einer chromatographischen Kammer in das Ionenaustauscherpapier wie üblich eingesogen. Vor dem Versuch wurde in die Kammer eine Schale mit Aceton und Wasser (3 : 2) gestellt. Die Zonen erscheinen gut getrennt auf dem Chromatogramm (Fig. 2).

Beide eben erwähnten Sulfonamide sind auf dem Austauscherpapier durch eine unbesetzte Zone getrennt. Diese Erscheinung ist durch die Anwesenheit von Ammoniak verursacht worden, welcher der Lösung einen alkalischen Charakter verlieh. Der pH-Wert der Lösung übt nämlich einen erheblichen Einfluss auf die Zonenbildung aus. Die zu analysierenden Lösungen sollen schwach sauer reagieren. Der günstigste pH-Bereich liegt zwischen pH = 2 bis 6. Verhältnismässig konzentrierte, z.B. 2 N starke Säure, bewirkt Auswaschen des Sulfonamides aus dem Austauscherpapier. Auch alkalische Lösungen vermögen eine Wanderung der Zonen der Sulfonamide zu verursachen. Prontosil rubrum ist ausnahmsweise in dieser Hinsicht wenig empfindlich. Im Falle anderer Sulfonamide genügt schon ein pH = 7.5 um die Zonen in Bewegung zu bringen. Je höher der pH-Wert der Lösungen, um so weiter wandert die Zone und um so kleiner wird ihre Fläche.

Die Anwesenheit von Salzen in der Lösung kann eine normale Ausbildung der Zonen verhindern. Falls das molekulare Verhältnis von Sulfonamid zu Metallkation kleiner als 1 : 1 ist, beginnt eine Verschiebung der Zone. Hierbei wird die Zone unscharf und zu quantitativer Auswertung unbrauchbar. Kleinere Mengen von Salzen, die zum Beispiel als zufällige Beimengungen in Tabletten anwesend sind, haben keinen unerwünschten Einfluss auf die Ergebnisse der Bestimmungen. Auch dreiwertiges Eisenkation, das durch den Austauscher stark komplex gebunden wird, beeinträchtigt die Bestimmungen nicht. In diesem Falle bilden sich unmittelbar über den dunklen Eisenzonen die Zonen der Sulfonamide, deren Flächen den Mengen der Sulfonamide proportional sind.

Nicht nur die Beimengungen, sondern auch das Volumen der zu bestimmenden Lösung, die Geschwindigkeit mit welcher die Lösung den Streifen durchfliesst, die Temperatur und ähnliche Faktoren können die Zonenflächen beeinflussen. In den angeführten Versuchsbedingungen (pH, Volumen der Lösungen auf der Tüpfelplatte, Breite der Dochte, Prozentgehalt (10%) des Austauscherpapiers an Ionenaustauscher) wird bei Zimmertemperatur eine Vergrösserung der Flächen bewirkt. Deshalb schneiden auch die extrapolierten Geraden in Fig. 1 das Koordinatensystem nicht im Nullpunkt. Da in derselben Versuchsreihe auf alle Streifen des Austauscherpapiers alle Faktoren praktisch in gleicher Weise einwirken, ist der Mehrbetrag der Flächen konstant. Somit ist die erwähnte Erscheinung ohne Einfluss auf die Resultate, da die Standardlösungen und die zu bestimmende Lösung zugleich, also unter gleichen Bedingungen, auf das Ionenaustauscherpapier gebracht werden. Um den Einfluss der Beimengungen aufzuheben, sind wo möglich die Standardlösungen mit bekannten Mengen der analysierten Substanz zu vermischen, so wie es in der Analyse üblich ist. Die zahlreichen, schon durchgeführten Analysen beweisen, dass die Ausbreitung der Bestimmungen mittels Ionenaustauscherpapier auf Sulfonamide bestens begründet ist.

DANK

Für die Durchführung mancher Bestimmungen sei Herrn A. Jarczewski gedankt.

ZUSAMMENFASSUNG

Mikrogrammengen von Sulfonamiden werden mittels Ionenaustauscherpapier bestimmt. Diese neue Methode erfordert wenig Aufwand an Arbeit und eignet sich vorzüglich für grössere Reihen von Bestimmungen.

SUMMARY

The quantitative determination of microgram amounts of sulfonamides by means of paper impregnated with ion exchangers is described. This new method is a rapid and convenient one and is suitable for serial estimations.

RÉSUMÉ

Une méthode est décrite pour le microdosage des sulfonamides sur papiers échangeurs d'ions. Ce nouveau procédé est rapide et permet des dosages en série.

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DERIVATIVES OF 1,4-DIHYDROXYANTHRAQUINONE AS METAL INDICATORS IN THE TITRATION OF THORIUM WITH DISODIUM EDTA

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INTRODUCTION

According to WELCHER[1] Alizarin Red S [1,2-dihydroxyanthraquinone-3-sulfonic acid (sodium salt)] is the only anthraquinone dye that has been successfully used as an indicator in EDTA (ethylenediaminetetraacetic acid) titrations. The high degree of interference caused by thorium in the spectrophotometric determination of aluminum and beryllium with derivatives of 1,4-dihydroxyanthraquinone[2] led us to examine the possibility of using quinizarin derivatives as metal indicators in a titration of thorium with disodium EDTA. Two derivatives are recommended: 2-quinizarinsulfonic acid (Na-salt) and 2-phenoxyquinizarin-3,4′-disulfonic acid (di-K-salt); the latter is preferred.

Reagents

Disodium EDTA solution: Aqueous solutions of disodium EDTA were prepared from the reagent grade disodium salt and standardized against spectroscopically pure zinc metal using Eriochrome Black T as indicator. This titration was carried out at pH 10 with ammonium chloride–ammonium hydroxide buffer[1].

Standard thorium solution: Thorium solutions were prepared from the reagent grade thorium nitrate and standardized with disodium EDTA using Alizarin Red S as indicator[3].

EXPERIMENTAL

Detection of the equivalence point

When thorium is present in excess, in the presence of indicator, the solution is pink, the color of the thorium–indicator complex. At the equivalence point the color changes to yellow, the color of the *unreacted* indicator, as thorium is displaced from its pink complex with the indicator to form a stronger, colorless complex with EDTA. The color change is reversible.

Results and conclusions

It is possible to carry out EDTA titrations of thorium using the new indicators at a lower pH than is possible with Alizarin Red S. The applicable pH-ranges for the titrations as compared with Alizarin Red S are shown in Table I (see also Figs. 1 to 3).

The phenoxyquinizarinsulfonate–thorium complex retains its bright pink color to lower pH values than the Alizarin Red S–thorium complex. Below pH 2.1 the Alizarin Red S–thorium complex is not stable enough to produce a sharp color change. (Its color above pH 2 is bright pink but changes to brownish-red below this value). The sharpness of the equivalence points as indicated by the color changes decreases with increased acidity, due to greater dissociation of both the thorium–dye complex and the thorium–EDTA complex. If the greater dissociation of the thorium–EDTA

TABLE I

COMPARISON OF pH-RANGES FOR STOICHIOMETRIC TITRATION OF THORIUM WITH EDTA

Indicator	*Applicable pH-range for stoichiometric titration*
Alizarin Red S	2.2 to 3.4
2-Quinizarinsulfonic acid (sodium salt)	2.0 to 3.4
2-Phenoxyquinizarin-3,4′-disulfonic acid (dipotassium salt)[a]	1.4 to 3.4

[a] In practice a mixture of the mono and disulfonates was used and is satisfactory.

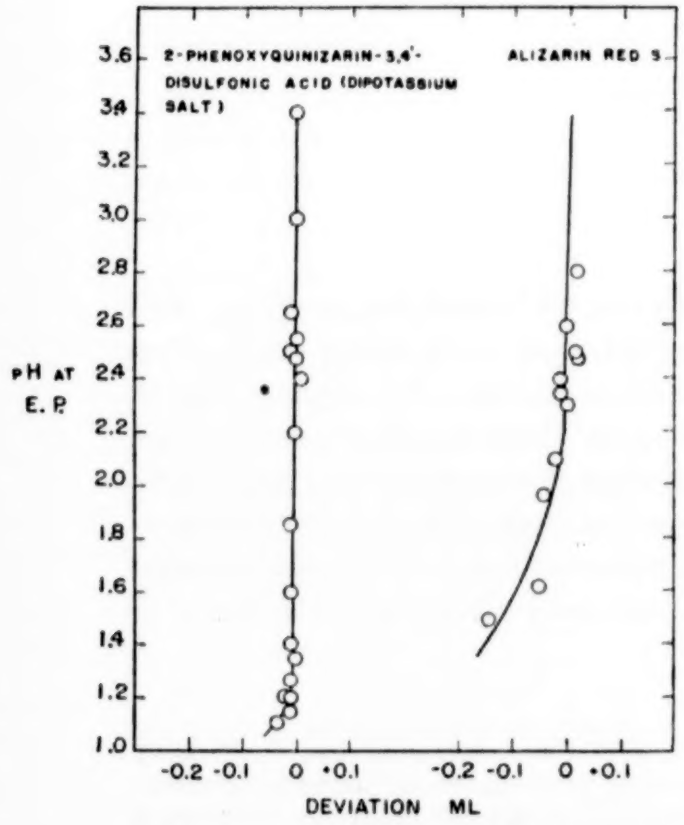

Fig. 1. pH range for stoichiometric titration of thorium with EDTA (with indicator). 0.012 *M* thorium at the E.P. titrated with 0.025 *M* EDTA, final volume about 20 ml.

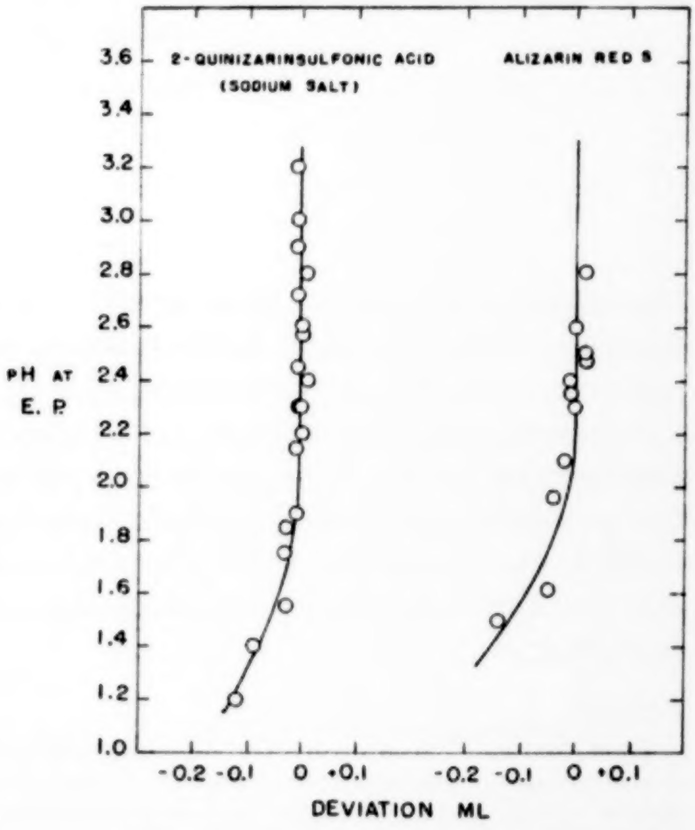

Fig. 2. pH range for stoichiometric titration of thorium with EDTA (with indicator). 0.012 *M* thorium at the E.P. titrated with 0.025 *M* disodium EDTA, final volume about 20 ml.

complex were the dominating factor, the deviation from the theoretical equivalence point would be positive. However, since the deviation at low pH is negative, it follows that the dissociation of the thorium–dye complex is the *major* contributor to the decrease in sharpness of the equivalence point.

Visual detection of the color change is, of course, a matter of color perception and depends on the concentration of both thorium and EDTA. The pH limits shown in Table I apply to a solution containing 0.012 *M* thorium at the equivalence point, the titrant being 0.025 *M* disodium EDTA. At greater dilutions, for example, 0.004 *M* thorium at the equivalence point, titrated with 0.025 *M* disodium EDTA, the lower pH limit for stoichiometric titration with the new indicators should move up by about 0.2 pH. Our observations were confirmed by an impartial person who carried out comparative titrations at pH 1.6 with both Alizarin Red S and the new phenoxyquinizarinsulfonate indicator. The latter indicator gave a much sharper color change at this pH than did the Alizarin Red S.

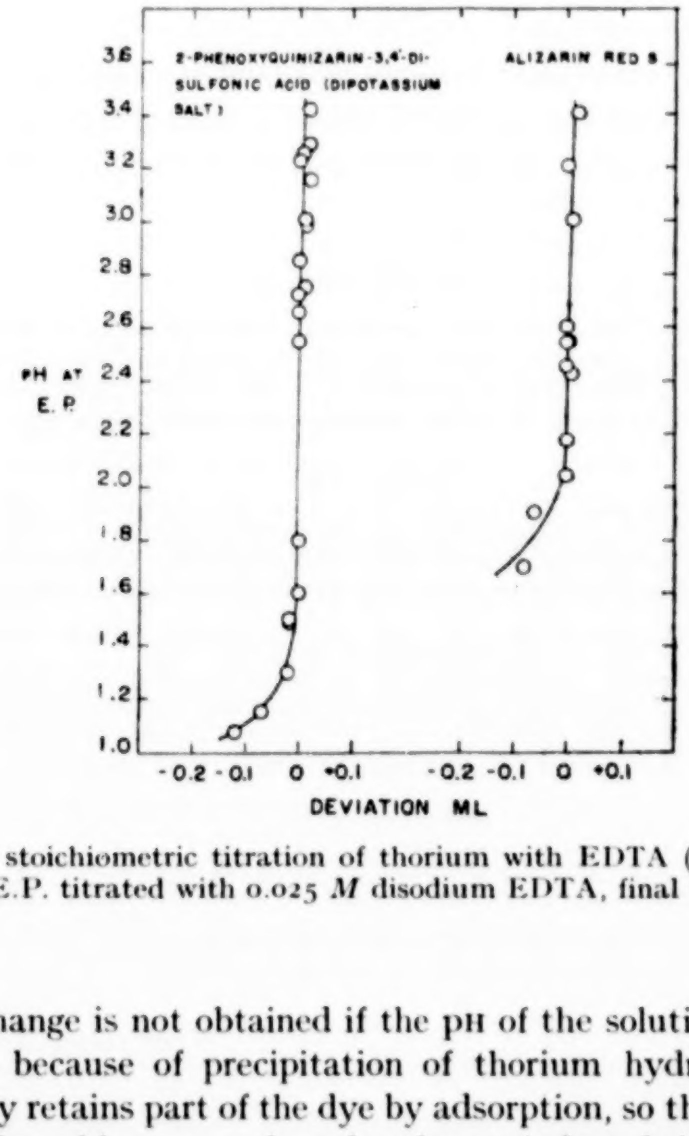

Fig. 3. pH range for stoichiometric titration of thorium with EDTA (with indicator). 0.004 *M* thorium at the E.P. titrated with 0.025 *M* disodium EDTA, final volume about 30 ml.

A sharp color change is not obtained if the pH of the solution is above 3.5 at the equivalence point because of precipitation of thorium hydroxide. The insoluble hydroxide probably retains part of the dye by adsorption, so that a clear yellow color does not result. When this occurs, the color change is from bright pink to light pink. Even so, since part of the thorium is precipitated and does not react immediately with EDTA, the correct equivalence point is not obtained. The upper pH limit is thus set at pH 3.5 by the precipitation of thorium hydroxide.

FRITZ AND FORD[3] found that the addition of a buffer to control the pH during the titration of thorium with EDTA, using Alizarin Red S as indicator, decreases the sharpness of the Alizarin Red S color change. Since no buffer is present, the narrow pH range required for the titration using Alizarin Red S makes the adjustment of pH a problem. Moreover, the titration of thorium with EDTA liberates two equivalents of hydrogen ions per equivalent of thorium complexed.

Within the recommended pH ranges, all three indicators (compared in Table I) produce very similar color changes from pink to yellow when thorium is titrated with EDTA. Titrations using 2-phenoxyquinizarin-3,4′-disulfonic acid (dipotassium salt) should require less attention to the regulation of pH than those with Alizarin Red S. In other respects the titration is the same as that described by FRITZ AND FORD[3]. The effects of possible interferences have not been investigated because qualitatively, at least, they will be similar to those encountered using Alizarin Red S. Interferences are discussed by FRITZ AND FORD[3] who recommend a preliminary mesityl oxide extraction to separate thorium from the rare earths and large amounts of fluoride and phosphate.

Precision

The precision (2σ) of titrations using the new indicators shown in Figs. 1 and 2 is about 2 parts per thousand and in Fig. 3 about 3 parts per thousand thorium. This represents an error of about 0.1 mg in the titration of 55.7 mg and 27.8 mg thorium, respectively.

SUMMARY

2-Quinizarinsulfonic acid (sodium salt) and 2-phenoxyquinizarin-3,4′-disulfonic acid (dipotassium salt) can be successfully used as metal indicators in the titration of thorium with disodium EDTA. The latter compound is recommended in preference to the former and Alizarin Red S as an indicator because it permits the titration to be made over a wider pH-range.

RÉSUMÉ

Deux indicateurs sont proposés pour le titrage du thorium au moyen de l'éthylènediaminotétracétate disodique: le sel de sodium de l'acide quinizarinesulfonique-2 et le sel dipotassique de l'acide phénoxy-2-quinizarine disulfonique-3,4′. L'emploi de ce dernier est recommandé.

ZUSAMMENFASSUNG

Zur komplexometrischen Bestimmung von Thorium mit Aethylendiaminotetraessigsäure (Na-Salz) eignen sich 2-Chinizarinsulfosäure (Na-Salz) und 2-Phenoxychinizarin-disulfosäure-3,4′ (K-Salz), wovon letztere wegen der geringeren pH Abhängigkeit bevorzugt wird.

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GRAVIMETRIC DETERMINATION OF GOLD (III) BY 2-MERCAPTOACETIC (THIOGLYCOLLIC) ACID

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The widely applied method for the gravimetric estimation of gold is the reduction to its elemental state and weighing in this form. The chloroacid complex of gold is reduced by a wide variety of both organic and inorganic reagents[1–5]. In many cases the metal separates from dilute solutions in such a finely divided state that it is not completely retained by the finest filter papers. Ferrous sulfate and sulfur dioxide cause complete precipitation over a wide range of acidity and do not require complete elimination of nitric acid. Oxalic acid has been quite commonly used but it requires elimination of nitric acid and closer control of acidity than the above two. BEAMISH *et al.*[6] recommended the use of hydroquinone in cold solution. The metallic gold separates as relatively large particles and can be filtered easily. However, difficulties have been encountered in the transference of traces of solid to the filter as the metallic gold has a tendency to stick to the sides of the beaker.

A number of organic reagents precipitate gold quantitatively which can be easily transferred and filtered without loss. Unfortunately most of these compounds do not have a constant composition or at least cannot be washed free of impurities. This necessitates ignition and weighing as metal sacrificing the advantages of a favorable weight factor. Among such reagents are tetramethyl ammonium chloride[7], dimethylglyoxime[8], mercaptobenzenethiazole[9,10], 2-mercaptobenzimidazole[9], and thioanilide[11]. HARVEY AND YOE[12] have reported the use of the sodium salt of N-(N-bromo-C-tetradecyl betanyl)-C-tetradecyl betaine as a reagent. The precipitate obtained is dried at 85° and weighed directly. MAHR AND DENCK[13] have used Reinecke salt for the precipitation. Au^{+3} is first reduced to the univalent form by arsenite, precipitated by Reinecke salt and weighed directly drying at 110–120°.

Preliminary investigations showed that thioglycollic acid can be utilized for the gravimetric estimation of gold. SANT[14] has estimated zirconium using the reagent and it has also been used for the colorimetric determination[15] of Fe^{+3}.

Reagents and solutions

Thioglycollic acid: A 10% stock solution of thioglycollic acid was prepared (Evans Chemetics Inc.)

Gold chloride: Gold chloride (Baker Analyzed Reagent) solution was prepared in HCl and the gold content ascertained by the hydroquinone method.

Procedure

To an aliquot of gold solution enough hydrochloric acid was added to maintain the final acidity at 6 *N*. The solution was then diluted to 50 ml and 10–12 ml of thioglycollic acid stock solution was added slowly with constant stirring. The precipitate passes through a transient brownish and changes to white. It was kept over steam bath for 20–30 minutes when slowly it changes to yellowish color. After keeping aside for half an hour it was washed 5–6 times with 10–15 ml portions of distilled water and transferred over the sintered glass crucible. It was dried at 110–120° and weighed as $C_2H_3O_2SAu$. Digesting the precipitate over steam bath for an hour or so improves the filterability of the precipitate. The precipitate can also be filtered on a Whatman 40 filter paper and ignited to the metallic form and weighed. A representative set of data are presented in Tables I and II.

Results and discussion

A carbon, hydrogen and sulfur analysis of the thoroughly washed precipitate gave the following percentage composition by weight: C – 8.88, H – 1.13, S – 10.11, as compared to the calculated values C – 8.33, H – 1.4, S – 11.11.

TABLE I

ESTIMATION OF GOLD BY DIRECT WEIGHING OF THE THIOGLYCOLLATE COMPOUND

	Amount of gold in milligrams		*Difference*
	Thioglycollate method	*Hydroquinone method*	
1	6.01	6.05	—0.04
2	12.06	12.10	—0.04
3	15.20	15.13	+0.07
4	30.26	30.26	0.00
5	45.49	45.39	+0.10
6	75.70	75.45	+0.25

TABLE II

ESTIMATION OF GOLD BY IGNITION OF THE THIOGLYCOLLATE COMPOUND

	Amount of gold in milligrams		*Difference*
	Thioglycollate method	*Hydroquinone method*	
1	6.88	6.84	+0.04
2	13.70	13.68	+0.02
3	34.40	34.22	+0.18
4	41.32	41.33	—0.01
5	68.40	68.44	—0.04

The following metal ions do not interfere with the precipitation even when they are present in concentrations four times more than that of gold: alkaline earth metals, magnesium, manganese(II), beryllium, aluminum, cerium(III), cadmium, cobalt, nickel, antimony, bismuth, titanium, iron(II and III), tin(IV), osmium(VIII), iridium(III), ruthenium(III), rhodium(III), and palladium(II). Platinum and zirconium precipitate with gold. Their interference can be eliminated by extracting gold from a chloride solution with isopropyl ether. Only two extractions of about 25 ml each are sufficient to extract gold completely from a 6 *N* HCl solution. The extracted layer is treated by 6 *N* HCl on a steam bath to bring the gold content back to the aqueous phase. This can subsequently be treated by the procedure already described.

The estimations can be carried out efficiently over a range of acidity of 2–10 *N*

HCl. Sulfuric acid cannot be tolerated but small amounts of nitric acid do not interfere with the analysis. Sodium or ammonium thioglycollates can also be used for precipitation instead of the pure acid. Excess addition of the reagent has no adverse effect on the precipitation. It is probable that Au^{+3} is first reduced to Au^{+} which is precipitated as thioglycollate. A study on the probable mechanism of precipitation and the structure of the compound is in progress. Among the advantages of the method are the favorable weight factor, easy transference and filtration of the precipitate and commercial availability of the reagent.

ACKNOWLEDGEMENTS

The author expresses his indebtedness to Boyd Professor PHILIP W. WEST for providing research facilities and his interest in the work. Thanks are also due to Evans Chemetics Inc., New York, for a gift sample of thioglycollic acid.

SUMMARY

Gold(III) can be quantitatively determined by precipitation in a 6 N HCl medium by thioglycollic acid. 6 to 60 milligrams of gold can be estimated within an error of $\pm 0.5\%$. Among the advantages of the method are favorable weight factor, easy transference and filtration of the precipitate and commercial availability of the reagent.

RÉSUMÉ

L'or peut être dosé gravimétriquement par précipitation au moyen de l'acide thioglycollique. Cette méthode présente de nombreux avantages.

ZUSAMMENFASSUNG

Die gravimetrische Bestimmung von Gold kann mit Hilfe von Thioglycolsäure erfolgen. Die Vorteile der Methode werden beschrieben.

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DETERMINATION OF CARBON ON NON-CONDUCTING CATALYSTS BY INDUCTION HEATING–CONDUCTOMETRIC METHOD

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Many catalysts used in petroleum processing are sensitive to small amounts of contaminants. One such material is carbon. To some types of synthetic catalysts, small amounts of carbon affect activity and/or selectivity appreciably; thus a rapid analytical procedure is needed to predict process controls. The search for a rapid procedure for determining total carbon on synthetic catalyst resulted in the development of a method which involves combustion followed by conductometric determination of the carbon dioxide formed.

Carbon on catalyst is generally determined by burning it in a resistance furnace and measuring the CO_2 evolved by gravimetric or volumetric methods. These methods proved inadequate because carbon trapped in catalyst pores could not be burned without first grinding the sample. This was time-consuming and, in addition, grinding did not necessarily release all of the carbon.

High frequency induction heating has also been used to burn carbon and it offered the advantage of higher temperatures whereby the sample is melted and entrapped carbon is exposed to oxygen. PEPKOWITZ[1] employed it in conjunction with a freeze-out technique for isolation of carbon dioxide, HOLLER *et al.*[2], absorbed the CO_2 in Ascarite, and SIMONS *et al.*[3], developed a high frequency combustion–volumetric method. All of these procedures were applied to metals and were not applicable directly to non- or low-conducting materials. In addition, the techniques used to measure the carbon dioxide involved were either time-consuming, too sensitive to operator error for control work, or not applicable in the range below 0.1% carbon.

This paper describes a rapid and reasonably precise method for determining total carbon in non-conducting catalysts or other solids. The carbon dioxide evolved from the high frequency furnace is absorbed in dilute barium hydroxide. The change in conductivity of this solution is directly proportional to the amount of carbon dioxide absorbed.

Apparatus

A simple schematic diagram of the apparatus is shown in Fig. 1 and a photograph is shown in Fig. 2. (1) High frequency induction furnace, equipped with "Vycor" glass combustion tube. A Lindberg Model LI-501F was used for this work. Other suitable makes and models are available. (2) Conductometric carbon determinator, Leco Model 515, was employed for the finishing step.

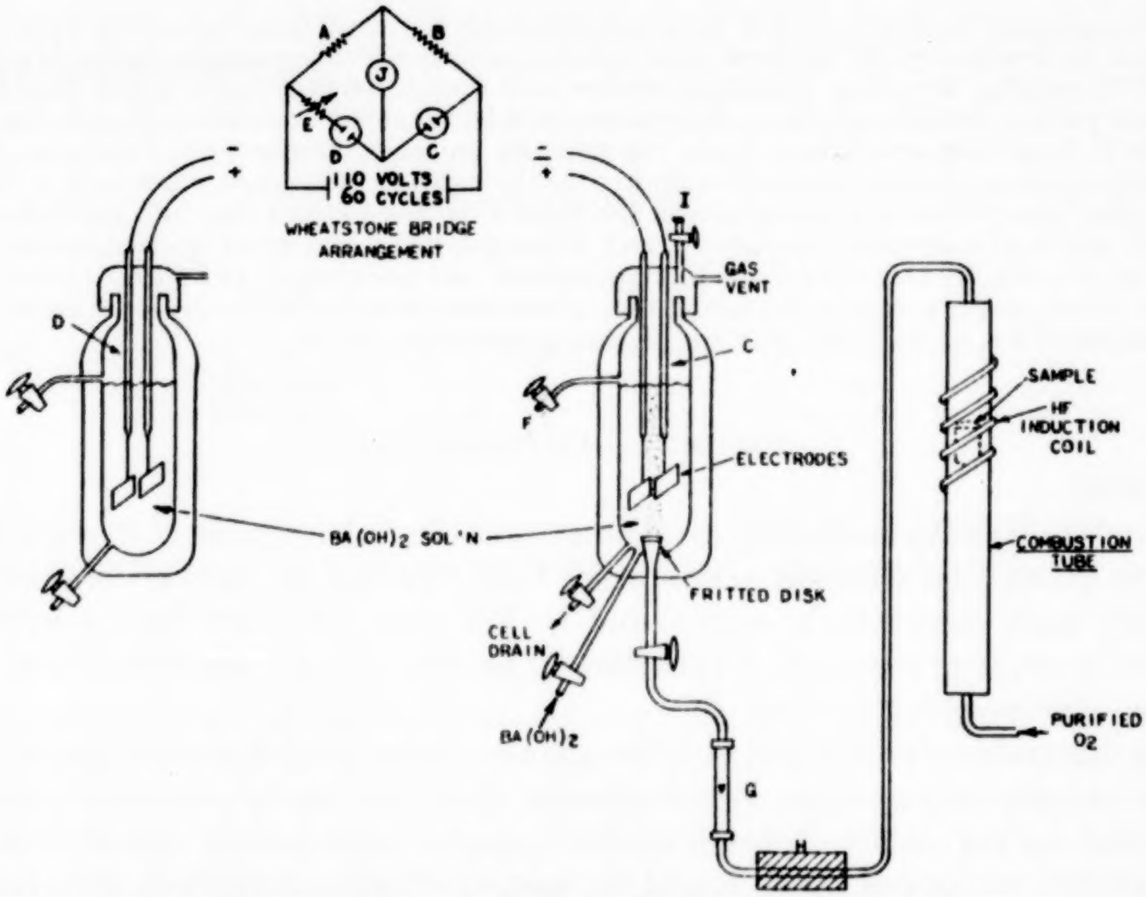
A
B
J
E
D
C
110 VOLTS
60 CYCLES
WHEATSTONE BRIDGE
ARRANGEMENT
−
+
D
−
+
I
GAS
VENT
C
F
SAMPLE
HF
INDUCTION
COIL
ELECTRODES
BA(OH)2 SOL'N
COMBUSTION
TUBE
FRITTED DISK
CELL
DRAIN
BA(OH)2
PURIFIED
O2
G
H

Fig. 1. Schematic diagram of apparatus. (A) fixed resistor; (B) fixed resistor; (C) measuring cell; (D) reference cell; (E) variable resistor; (F) cell leveling outlet; (G) rotameter; (H) sulfur scrubber; (I) wash solution inlet; (J) cathode ray tube.

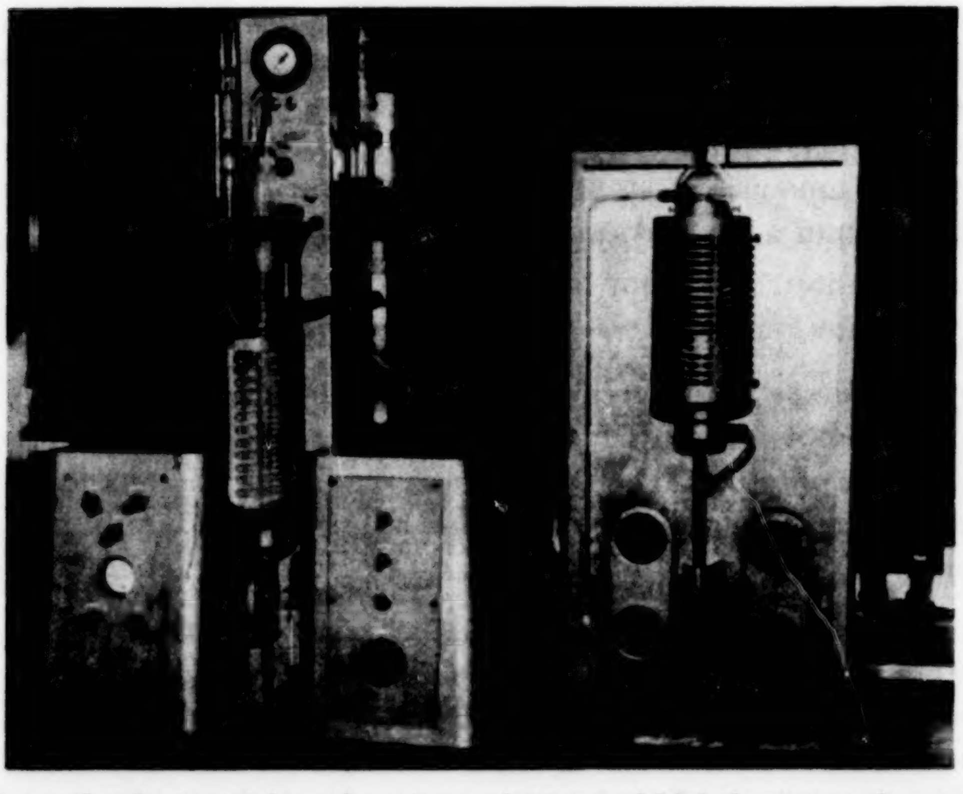

Fig. 2. Conductometric carbon determinator and high frequency furnace.

Reagents

Oxygen, prepurified grade, fed from a gas cylinder equipped with a reduction valve. It is further purified by passing it over an oxidation catalyst and then through Ascarite and a drying agent to remove carbon dioxide and water. Manganese dioxide, granular, non-carbon dioxide absorbing, Leco 501C. Iron chip accelerator, Leco 160 and tin, 20 mesh, carbon free, Leco 155. Barium hydroxide solution: Bubble carbon dioxide-free air through 16 l of distilled water for 1 h. Dissolve 15 g of $Ba(OH)_2 \cdot 8\ H_2O$ (reagent grade) in 500 ml of CO_2-free water. Filter into the CO_2-free 16 l of water previously prepared. Dissolve 2 g of Knox gelatin in 500 ml of warm CO_2-free water. Add 5 ml of 2-ethylhexanol. Add this to large volume and bring up to 18 l with CO_2-free water. Stopper bottle, shake contents throughly, then allow solution to stand for one week before using. NBS Standard No. 57 (Silicon), used for preparing calibration curve.

RECOMMENDED PROCEDURE

Calibration

Assemble apparatus according to manufacturer's instructions and as shown in Fig. 2. Turn on power and constant temperature bath switches on carbon determinator. Carefully place electrodes in cells C and D. Fill both cells with barium hydroxide solution to leveling outlet H. Adjust flow of oxygen to 250–300 ml/min and purge system while weighing sample.

To a dry carbon-free ceramic crucible add one scoop (1/4″ diameter by 1/4″ deep) of iron and one scoop of tin. Weigh crucible, then add enough standard sample to give about 0.2 mg carbon. Reweigh to obtain exact sample weight. Add an additional scoop of iron and one of tin on top of the sample. Position crucible in "Vycor" glass combustion tube.

With oxygen flowing through the system, zero the decade reading on the Carbon Determinator and adjust lines on scope to coincide. Ignite sample for 5 min, then turn off furnace but continue flushing tube with oxygen. As oxygen flushes the combustion products from the furnace tube and into the scrubbing solution, the lines on the scope separate. Keep the lines together by increasing the decade (Ohms) reading. When all of the carbon dioxide has been absorbed in the barium hydroxide solution (total time is 10–15 min), the lines will no longer separate. Record this decade reading. Drain and rinse measuring cell with dilute HCl followed by water. Refill cell with barium hydroxide solution. Solution in the reference cell is changed whenever a new batch of barium hydroxide is put in use.

Burn increasing amounts of standard containing up to 0.6 mg carbon such as to permit construction of a calibration curve, decade reading *vs.* mg carbon.

Unknown samples

Unknown samples are analyzed in the same manner as described above. It has been found that 0.2-g samples are satisfactory. If samples much larger are taken, incomplete combustion is obtained. The final decade reading of the unknown is compared to the calibration curve in order to determine milligrams carbon burned.

A blank must be determined on the iron and tin and subtracted from values of the unknowns.

EXPERIMENTAL RESULTS

The precision of the method was established by repetitive analyses of plant samples. The standard deviation was found to be ±0.007% at the 0.07% carbon level. Accuracy was demonstrated by the determination of NBS standard samples. These data are presented in Table I.

TABLE I

ACCURACY OF METHOD

Sample	*No. of determinations*	*Carbon, wt.%*	
		Certified value	*Found*
NBS-101C	5	0.072	0.065
NBS-57	10	0.087	0.081

It should be noted that the application of this method did not require better precision than shown, thus ultimate precision was not sought and may be better than indicated.

DISCUSSION

The measuring system of the conductometric apparatus is essentially a Wheatstone bridge, as shown in Fig. 1. Resistances A and B are fixed while E is variable, having a range of 0–100 Ohms. C and D are the glass cells containing barium hydoxide solutions, D being the reference cell and C is the measuring cell. J is an amplified cathode ray tube which indicates the state of balance of the bridge.

In operation, the bridge is balanced $A/B = D/C$. When the sample is burned, the carbon dioxide produced is introduced into cell C. This decreases the conductivity of the barium hydroxide solution due to formation of barium carbonate. The bridge is again balanced using the variable resistance E so that $A/B = D + E/C$, E then being directly proportional to the amount of carbon present.

The calibration curve should be checked daily. Investigation has shown that calibration does not shift during a given day but only when the instrument is shut down and restarted. Repeated efforts to establish a stable calibration curve failed. However, part of the shift in calibration was found to result from handling the measuring electrodes which were removed between analyses in order to rinse the measuring cell. The shift was lessened appreciably by adding glass tube I, whereby the HCl and water could be placed into the measuring cell without moving the electrodes.

Lines on the cathode ray tube should be parallel. Some difficulty with keeping them parallel was encountered and was traced to small variations in resistors. This difficulty was easily eliminated by connecting ten-turn helipots across each electrode and adjusting their resistances until the lines were parallel.

Success of this procedure depends, of course, upon complete oxidation of carbon to carbon dioxide. This is determined largely by temperature and the availability of oxygen at time of ignition. The excess supply of oxygen is easily maintained by increasing the input as the sample burns. Also, oxidizing agents may be used if needed.

Temperature presents a problem when low-conducting samples are to be analyzed. A conducting material must be added in proper amounts to insure an adequate temperature for oxidizing the sample. Electrolytic iron[4] is suitable for this purpose. Tin is usually added to lower the melting point of iron. Various amounts of each were employed in burning synthetic catalysts and the amounts stated in the procedure were found to be optimum.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Esso Standard, Division of Humble Oil and Refining Company for permission to publish this work.

SUMMARY

A method is described for the determination of carbon in non-conducting synthetic catalysts. Carbon is oxidized in a high frequency induction furnace and the evolved carbon dioxide is absorbed in a solution of barium hydroxide. The change in conductivity of this solution is directly proportional to the carbon burned. The method is rapid and reasonably precise at the 0.05% carbon level.

RÉSUMÉ

Une méthode est décrite pour le dosage rapide du carbone dans des catalyseurs. On procède par combustion dans un four à induction, à haute fréquence. L'anhydride carbonique obtenu est absorbé dans une solution d'hydroxyde de baryum. La variation de conductibilité de cette solution est proportionnelle à la quantité de carbone brûlée. La méthode est rapide et d'une précision satisfaisante au niveau de 0.05% de carbone.

ZUSAMMENFASSUNG

Beschreibung einer Schnell-methode zur Bestimmung des Kohlenstoffs in Katalysatoren durch Verbrennung in einem Hochfrequenz-Induktionsofen. Das gebildete Kohlendioxyd wird in Barytlauge absorbiert und die Änderung der Leitfähigkeit gemessen; diese ist dem Kohlenstoffgehalt direkt proportional. Die Exaktheit der Methode ist bei 0.05% Kohlenstoffgehalt zufriedenstellend.

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THE THERMAL PROPERTIES OF SOME AMINE TETRAPHENYLBORON SALTS

8-QUINOLINOL AND ITS DERIVATIVES

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In dilute acid solutions, many aliphatic and aromatic amines form insoluble salts with the tetraphenylboron ion, $[B(C_6H_5)_4]^-$, having the composition, $AmH^+[B(C_6H_5)_4]^-$ where AmH^+ is the amine onium ion. These salts have been useful for the qualitative and quantitative estimation of the amines[1–6]. However, Crane[3] discovered that 8-quinolinol (oxine) forms a salt with the tetraphenylboron ion (TPB) which had the composition, 2 oxine: 1 TPB. On the basis of ionic charge considerations, the composition should be similar to that found for other amine salts, namely, 1 oxine: 1 TPB.

Wendlandt[7] has previously studied the thermal stability of the oxine-TPB salt and concluded, from the weight loss data, that one of the oxine molecules was held by weak crystal forces similar to that found for the uranium, thorium, and scandium oxine complexes[8]. However, further studies revealed that this was not the case. It is the object of this study to reinvestigate the thermal properties of the oxine-TPB salt as well as those formed by the derivatives of oxine.

EXPERIMENTAL

Reagents

5,7-Dichloro- and 5,7-dibromo-8-quinolinol were obtained from the Eastman Organic Chemicals Co., Rochester 3, N.Y. 5,7-Diiodo-8-quinolinol and 2-methyl-8-quinolinol were obtained from the Aldrich Chemical Co., Milwaukee, Wisconsin. The latter two compounds were repeatedly recrystallized from water–alcohol mixtures. Sodium tetraphenylboron was obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J. All other reagents used were of C.P. quality.

Thermobalance

The thermobalance used was similar to that described by CAMPBELL AND GORDON[9]. Sample sizes ranged in weight from 90–100 mg with a heating rate of 6.6° per min. Duplicate and in some cases triplicate runs were made on each compound.

Differential thermal analysis apparatus (DTA)

The DTA apparatus consisted of a furnace similar to that described by LODDING AND HAMMELL[10], a microvolt strip-chart recorder, and a furnace temperature controller previously described by WENDLANDT[11]. Sample sizes ranged in weight from 90–120 mg, using calcined alumina as the reference compound. A heating rate of 8.0° per min was employed with a recorder chart speed of 6 in./h.

Infrared studies

The infrared absorption spectra were obtained with a Perkin-Elmer, Model 112, single beam, double pass instrument. The fused KBr pellet technique was employed, using a salt to KBr weight ratio of 1 : 400.

TABLE I

ANALYSIS OF AMINE TETRAPHENYLBORON SALTS

Formula	*Color*	*m.p. °C*	*% Nitrogen*		*% Amine*	
			Theor.	*found*	*Theor.*	*found*
8-Quinolinol: $(C_9H_6NOH)_2HB(C_6H_5)_4$	green-yellow	198–9	4.59	4.63	47.70	47.30
2-Methyl-8-quinolinol: $(C_{10}H_8NOH)_2HB(C_6H_5)_4$	yellow	171–3	4.39	4.43	50.10	49.20
5,7-Dichloro-8-quinolinol: $(C_9H_4Cl_2NOH)_2HB(C_6H_5)_4$	yellow		3.75	3.74		
5,7-Dibromo-8-quinolinol: $(C_9H_4Br_2NOH)_2HB(C_6H_5)_4$	yellow		3.03	3.89		
5,7-Diiodo-8-quinolinol: $(C_9H_4I_2NOH)_2HB(C_6H_5)_4$	yellow		2.51	2.62		

Preparation of compounds

The 8-quinolinol and 2-methyl-8-quinolinol TPB salts were prepared according to the procedure described by CRANE[3]. A slight modification was necessary with the

5,7-dihalo-derivatives. The 5,7-dihalo-8-quinolinols were dissolved in acetone–water–hydrochloric acid mixtures (25% acetone for 5,7-dichloro-; 50% for 5,7-dibromo-; and 75% for 5,7-diiodo-) which were about 0.3 *M* in acid concentration. Upon addition of the sodium-TPB solution (0.6% solution), yellow precipitates of the 5,7-dichloro- and 5,7-dibromo-8-quinolinol TPB salts were obtained while the 5,7-diiodo-8-quinolinol compound was obtained only after most of the solvent had been evaporated.

The compounds were analyzed for nitrogen content by the Dumas method as given in Niederl and Niederl[12]. The 8-quinolinol and 2-methyl-8-quinolinol contents were determined by a bromometric procedure[13]. The results of the analyses are given in Table I.

RESULTS AND DISCUSSION

The thermal stability curves, as determined on the thermobalance, are given in Fig. 1. The DTA curves for the amine TPB salts and the free amines are given in Figs. 2 and 3, respectively.

The thermal decomposition curves can be divided into two groups; (*a*) Group I: those for the 8-quinolinol and 2-methyl-8-quinolinol TPB salts; and (*b*) Group II: those for the 5,7-dihalo-8-quinolinol TPB salts. In Group I, weight losses were observed at much lower temperatures than those for Group II. These weight losses began at 50° for the 8-quinolinol salt and 70° for the 2-methyl-derivative. For Group II, minimum decomposition temperatures ranged from 127° to 203°, for the 5,7-dibromo- and 5,7-diiodo-derivatives, respectively.

The first weight loss for the Group I compounds appears to be due to sublimation

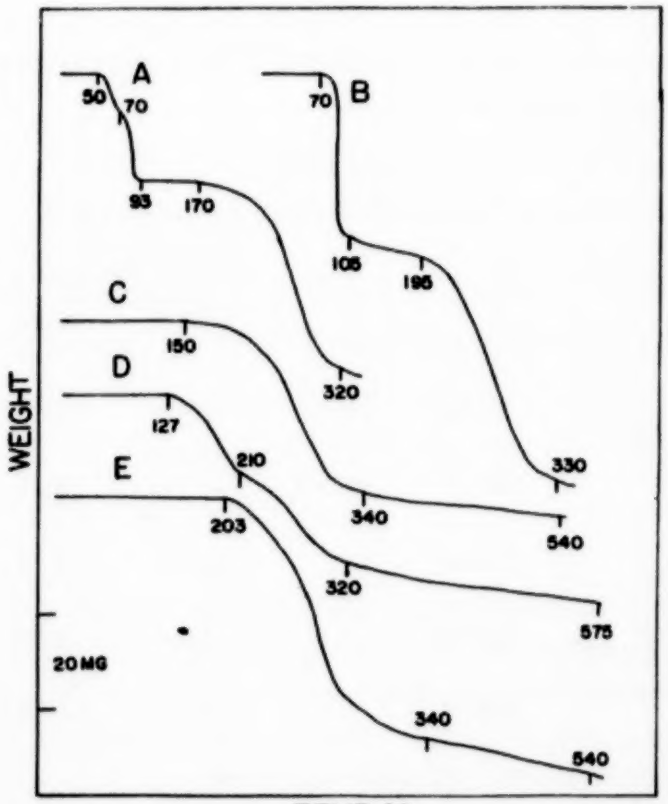

Fig. 1. Thermal decomposition curves of amine tetraphenylboron salts. (TPB is the tetraphenylboron ion.) A. 8-Quinolinol TPB, B. 2-Methyl-8-quinolinol TPB, C. 5,7-Dichloro-8-quinolinol TPB, D. 5,7-Dibromo-8-quinolinol TPB, E. 5,7-Diiodo-8-quinolinol TPB.

of the initial compound, and not to a thermal decomposition reaction. This was proved by the following methods: (*a*) a small sample of the sublimate was collected and found to melt at the same temperature as the initial compound; (*b*) infrared spectra were identical for the initial sample and the residue after the first weight loss; (*c*) nitrogen content analysis on the residue had the same value as the initial compound. This behavior is not consistent with the results reported by HOWICK AND PFLAUM[14] for the lower molecular weight amine TPB salts. Also, the compounds do not lose the extra molecule of amine as previously suggested[7].

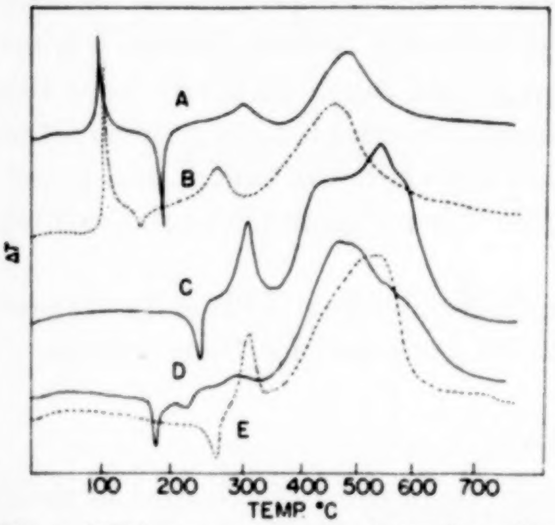

Fig. 2. DTA curves of amine tetraphenylboron salts. A. 8-Quinolinol TPB, B. 2-Methyl-8-quinolinol TPB, C. 5,7-Dichloro-8-quinolinol TPB, D. 5,7-Dibromo-8-quinolinol TPB, E. 5,7-Diiodo-8-quinolinol TPB.

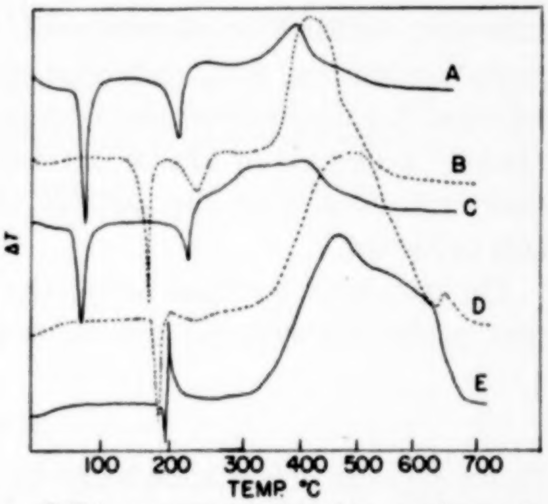

Fig. 3. DTA curves of the free amines. A. 8-Quinolinol, B. 5,7-Dichloro-8-quinolinol, C. 2-Methyl-8-quinolinol, D. 5,7-Dibromo-8-quinolinol, E. 5,7-Diiodo-8-quinolinol.

The DTA curves give some rather interesting information concerning these first weight losses for the Group I compounds. Apparently, an exothermic crystalline phase transition or rearrangement takes place in which a portion of the initial compound sublimes. However, a simple sublimation reaction is normally an endothermic reaction, *i.e.*, the peak would be in the opposite direction, but this could be obscured by the larger exothermic reaction. After this first unusual energy change, the residual material decomposes in a manner similar to the Group II compounds.

The DTA curves for the 8-quinolinol TPB compounds differ greatly from those reported for the lower amine salts[14]. All of the latter compounds give exothermic peaks, all of them being found under 300°. In this investigation, with the exception of Group I compounds, broad exothermic peaks were observed up to 700°. This may be due to the different equipment used in the determination of the DTA curves or it may be due to inherent differences in the two series of compounds.

Although a decomposition mechanism of the amine TPB salts has been postulated, it was first suspected that the free amines were formed during the thermal decomposition process. To determine if this was the case, the free amines were examined by DTA and their curves compared to the amine TPB salts. As can be seen, there is little similarity between the curves. The free amines exhibited endothermic peaks corresponding to the fusion of the compound, then, except for the 5,7-dibromo- and 5,7-diiodo-derivatives, another endothermic peak followed by a broad exothermic peak. 5,7-Diiodo-8-quinolinol released voluminous amounts of free iodine when it decomposed which may account for its unusual first peak which began as an endothermic and ended as an exothermic peak.

From the thermal decomposition curves, it is apparent that the 1 : 1, amine to TPB, salts do not exist. Instead, some type of a crystalline rearrangement takes place (with 8-quinolinol and 2-methyl-8-quinolinol TPB) in which a portion of the salt sublimes, rather than decomposes. It is difficult to postulate a structure for a compound exhibiting such behavior since the properties are much different from the solvated 8-quinolinol thorium, scandium, and uranium(VI) complexes. Obviously, the "extra" molecule of amine is retained by quite strong chemical bonds, and is not easily removed from the salt. To our knowledge, no other 8-quinolinol salts exhibit this behavior.

The excellent thermal properties of the 5,7-dihalo-8-quinolinol TPB salts suggest that perhaps a suitable gravimetric method could be developed for these amines.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge Dr. A. J. BARNARD, Jr. of the J. T. Baker Chemical Co., for the samples of sodium tetraphenylboron.

SUMMARY

The thermal decomposition of the tetraphenylboron salts of 8-quinolinol, 2-methyl-, 5,7-dichloro-, 5,7-dibromo- and 5,7-diiodo-8-quinolinol were studied on the thermobalance and by differential thermal analysis. The 8-quinolinol and 2-methyl-8-quinolinol salts begin to sublime at much lower temperatures than the corresponding 5,7-dihalo-derivatives. The excellent thermal stability of the 5,7-dihalo-8-quinolinol salts suggests that they may be useful for the gravimetric determination of the free amines.

RÉSUMÉ

Les auteurs ont étudié la décomposition thermique de quelques dérivés du tétraphénylbore (TPB) : TPB-hydroxy-8-quinoléine, TPB-méthyl-2-hydroxy-8-quinoléine, TPB-dichloro-5,7-hydroxy-8-quinoléine, TPB-dibromo-5,7-hydroxy-8-quinoléine, TPB-diiodo-5,7-hydroxy-8-quinoléine, au moyen de la thermobalance et par analyse thermique différentielle.

ZUSAMMENFASSUNG

Untersuchung über die thermische Zersetzung der Tetraphenylborsalze von 8-Oxychinolin, 2-Methyl-, 5,7-Dichlor-, 5,7-Dibrom-, und 5,7-Dijod-8-oxychinolin mit Hilfe der Thermowage und differentialthermische Analyse. Die 5,7-Dihalogenderivate zeigen sehr gute thermische Stabilität.

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ANALYSIS OF MCPA/TBA HERBICIDE FORMULATIONS

II. A GAS–LIQUID CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF 4-CHLORO-2-METHYL PHENOXYACETIC ACID

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In part I of this series[1], we have described the liquid–liquid chromatographic determination of 236 in MCPA/TBA herbicides. It was also necessary to determine 4C2M in these formulations and this part describes the method.

INTRODUCTION

It was shown in part I that a partial separation of MCP acids from the chlorobenzoic acids is achieved by the chromatographic method used for determination of 236.46C-2M, 4C2M and 6C2M* are partially resolved from each other and completely from 2M, but the three former acids appear in the "other acids" fraction of the liquid–liquid chromatogram, 2M appearing just before the "tetrachloro acid" fraction. The method is therefore unsuitable for determination of 4C2M in MCPA/TBA herbicides.

Published methods for determination of 4C2M in MCPA herbicides include isotope dilution[2], ultra-violet spectrophotometric[3,4], infra-red spectrophotometric[5], liquid-liquid chromatographic[6,7], differential refractometric[8] and gas–liquid chromatographic[9] procedures. A combination of the U.V. and L.L.C. methods[10] has also been used. It seemed likely that the isotope dilution method would require considerable modification before it could be applied to MCPA/TBA mixtures. With the large proportion of acids other than 4C2M present, infra-red and ultra-violet spectrophotometric and differential refractometric procedures were likely to be difficult to apply without at least partial separations beforehand. Preliminary experiments with modifications of the L.L.C. methods[1,6,7] showed that it would probably be difficult to avoid one or more of the chlorobenzoic acids eluting together with 4C2M.

It is known that the four MCP acids can be readily separated and determined as their methyl esters by gas–liquid chromatography[9]. It is also stated in the literature[11] that *ortho*-halogenated benzoic acids are extremely difficult to esterify by the FISCHER–SPEIER method. It was therefore proposed to ease the likely problem of TBA interference in MCPA gas–liquid chromatography by esterifying with methanol under suitable acidic conditions for the complete conversion to methyl esters of all the MCP acids while all the 26 substituted chlorobenzoic acids remain unesterified. Conditions of GLC would then be sought to avoid interference of the esterified TBA (not di-*ortho* substituted) with 4C2M determination.

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* **Abbreviations are the same as those used in part I (Ref.[1]).**

EXPERIMENTAL

(*1*) *Preparation of methyl ester*

For ease of handling, the use of methanol–sulphuric acid was preferred to the FISCHER-SPEIER method. The MCP acids were esterified by the following process:

1 g of the acid or a mixture of acids was dissolved in 20 ml of purified methanol and 1 ml of concentrated sulphuric acid added. This mixture was refluxed for four hours. The resultant mixture was transferred quantitatively into 100 ml of distilled water and the acids and esters extracted with methylene chloride. Sufficient sodium bicarbonate was then added to neutralize sulphuric acid and any free acids remaining. The two layers were separated, the aqueous layer re-extracted twice with methylene chloride, the solvent layers combined and solvent removed.

Normally this mixture would be applied directly to the chromatographic column but in order to check the extent of esterification of the MCP acids, further work was carried out. In this case, the bicarbonate layer was retained, reacidified and the organic acids extracted with ether. Finally the ether layer was dried over sodium sulphate, evaporated to dryness, dissolved in a little ethanol and titrated with 0.01 *N* sodium methylate[12] using bromothymol blue indicator. Owing to their significant vapour pressure, it was not possible to weigh small amounts of the esters. The recovered esters in the solvent layer were therefore saponified in alcoholic caustic potash and the acids recovered by acidifying the cooled liquid and extracting with ether. The liberated acids were dissolved in neutral ethanol and titrated with 0.2 *N* sodium hydroxide.

The result of this work is shown in Table I and demonstrates that the degree of esterification is reasonably consistent for all MCP acids and approaches 100%.

The esterification technique was also investigated with pure acids typical of those present in technical TBA. Results obtained with 245, 24, and 236 are also shown in Table I.

TABLE I

DEGREE OF ESTERIFICATION BY METHANOL–SULPHURIC ACID
(4 h reflux)

	Recovered from solvent layer	*Recovered from bicarbonate layer*
2M	98%	0.4%
4C2M	98%	1.3%
6C2M	97.8%	2.1%
46C2M	96.5%	2.9%
245	97.5%	2.9%
24	96%	2.5%
236	<0.1%	99%

The degrees of esterification of all other acids were not investigated in detail but on theoretical grounds it was expected (*a*) that the other di-*ortho* substituted acids would not be esterified to any significant extent and (*b*) that the remaining acids would be esterified partially or completely. A check on other typical di-*ortho* substituted acids was carried out; 26 and 2356 were treated by the normal esterification procedure followed by gas chromatography of the "esterified" fraction. No ester could be detected in the positions determined by chromatography of the appropriate esters made using the diazomethane procedure. This indicated less than 0.1% conversion to ester under the conditions used. It therefore seemed reasonable to assume that, as predicted, none of the di-*ortho*-substituted acids would interfere with the proposed gas chromatography of the esterified sample.

All the results given in this paper were carried out using a standard reflux time of 4 h. Subsequent work has shown that esterification of 4C2M acid reaches a constant value of 98% at 30 min refluxing and a time of 1 h is now preferred for the esterification stage.

(2) *Selection of column*

Experimental gas chromatography was conducted using the methyl esters, prepared as in (1), of pure chlorobenzoic and MCP acids and also using methyl esters prepared from technical TBA and technical MCPA.

Initial trials were run with 2 metre Nansa HS* columns which had been recommended[9] for analysis of MCPA herbicides. The 234 methyl ester peak coincided with that of 4C2M, although a separation of 235 and 245 from 4C2M was obtained.

A 2-metre silicone oil column (M & B silicone oil) gave identical retention times for 235, 245 and 4C2M but separated 234 from 4C2M. With neither of these columns did any of the other chlorobenzoic and MCP acids interfere.

Using a 1-metre Apiezon grease M column (25% on 40–60 mesh Celite 545**) a partial separation of 235 + 245, 234 and 4C2M was obtained.

The chromatogram demonstrated a triple peaked hump and calculation showed that complete separation would be achieved if the column were doubled in length (producing a very nearly doubled platage). The 2-metre Apiezon M column produced a satisfactory isolation of the desired peak. A typical chromatogram of a commercial formulation is shown in Fig. 1. It should be noted that any chlorocresols present are at least partially extracted and therefore chromatographed. It has been suggested by HADDOCK *et al.*[9] that some minor impurities may have the same retention factor as 4C2M and this caused high results to be obtained when using GLC with their Nansa columns. We have had no evidence in our work of any such interfering minor impurities. Glycollic acid is eliminated in the initial extraction. Retention factors from different columns are shown in Table II.

(3) *Quantitative determination*

Since some of the TBA acids are not, or are only partially, esterified, methods of determination using internal normalisation are impracticable. It was therefore decided to use an internal standard method. Ethyl benzoate is readily available and was found to be suitable. On chromatography it appears before 2M and after the monochlorobenzoic acid esters. Traces of relatively volatile solvents present in the commercial herbicides do not interfere. The first step was the standardisation of ethyl benzoate

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* Supplied by Marchon Products Limited, Whitehaven.

** Supplied by Johns Manville Limited, Artillery Row, London.

TABLE II

RETENTION FACTORS OF METHYL ESTERS *cf.* 4C2M METHYL ESTER AS 1.00 AT 190°

Acid	*Nansa HS*	*Silicone oil*	*Apiezon M*
2	0.26	—	0.26
3			
4			
23	0.61	0.69	0.54
24	0.38	0.60	
25	0.42	0.58	
26	0.36	0.55	0.44
34	0.59	0.69	0.54
35	0.37	0.54	
234	0.95	1.15	1.37
235	0.77	0.95	1.09
236	0.55	0.92	0.89
245	0.67	1.00	1.15
246	0.52	0.90	0.73
345	—	—	—
2345	1.8	1.95	2.6
2346	—	—	—
2356	0.73	1.45	1.50
46C2M	1.37	1.29	1.65
4C2M	1.00	1.00	1.00
6C2M	0.63	0.81	0.76
2M	0.36	0.50	0.38
4-Chlorocresol	0.95	0.3	0.45
6-Chlorocresol	0.11	0.17	0.15
4,6-Dichlorocresol	0.32	0.36	0.37

against 4C2M. This was carried out by esterifying a known weight of the pure acid (m.p. 119.5–120°) with methanol–sulphuric acid as described above, separating the resulting ester from the other components of the mixture, and adding a solution containing a known weight of ethyl benzoate in methylene chloride. The solution was evaporated to dryness and 3 μl of the resultant mixture chromatographed on a 2-m Apiezon M column using the conditions described later under "Method".

The actual ratio of peak areas varied slightly with the ethyl benzoate used as most commercial samples examined, plainly contained small variable amounts of water, methyl benzoate and isopropyl benzoate. It was therefore necessary to re-calibrate for each fresh batch of ethyl benzoate used. The standardisation was repeated with one batch of ethyl benzoate until a statistical assessment of precision could be made and this was found to be ± 1.8% (95% confidence limits).

The method was checked by examination of a technical MCPA formulation of which the 4C2M content had been well established by analysis using the liquid–liquid chromatographic method[7]. These results are shown in Table III.

The method was next applied to synthetic mixtures containing known amounts of both technical MCPA and technical TBA. The sample of technical MCPA analysed (see Table III) was mixed with different proportions of technical TBA (containing about 50% 236). These mixtures cover a range of ratios 4C2M : 236 wider than that likely to be encountered in commercial formulations. The results are shown in Table IV, the 4C2M content being expressed in terms of the calculated percentage present in the original technical MCPA used, are comparable with those in Table III.

TABLE III

COMPARISON OF RESULTS ON TECHNICAL MCPA (WITHOUT TBA) BY LIQUID–LIQUID CHROMATOGRAPHY AND PROPOSED METHOD

Content by L.L.C.	*Content by proposed method*
22.8% w/w	23.0% w/w
	22.7% w/w
	22.5% w/w
	22.8% w/w
	22.7% w/w
	22.5% w/w

The results obtained in Tables III and IV were obtained using a slightly different extraction procedure from that finally recommended in "Method". Methylene chloride was used instead of ether in the initial extraction of acids from the acidified formulation. This was subsequently shown to result in slight but consistent loss of 4C2M. The results in Tables III and IV are corrected for this loss. A correction is not required when ether is used for the acid extraction.

TABLE IV

ANALYSIS OF MCPA/TBA MIXTURES

Approximate proportion		*Content of 4C2M by proposed method*
236	*4C2M*	
2	1	22.5% w/w
1	1	22.7% w/w
		23.2% w/w
1*	2*	23.0% w/w
		23.1% w/w
		23.0% w/w
		22.8% w/w
1	4	22.6% w/w
		22.5% w/w
1	8	22.9% w/w
		22.6% w/w

* Represents commercial formulation.

In all the gas chromatography described in this paper, hydrogen was used as a carrier gas. Nitrogen has distinct advantages because of its safety and of the increased platages obtained due to its much lower diffusion coefficient. We have reduced the hazard of using hydrogen at relatively high temperature by (1) always passing nitrogen through the columns before and after use of hydrogen (2) maintaining an atmosphere of carbon dioxide in the oven of the instrument as a precaution against leaks.

The decreased platage with hydrogen is more than offset by the advantage of the much higher detector sensitivity which can be used. With katharometers and more particularly thermistor detectors at high temperatures, lower flow rates must be used with nitrogen[13] with consequent loss of efficiency.

METHOD

Apparatus

A Perkin Elmer Model 116 Fraktometer was used for the determination with a 1 mV f.s.d. recorder (Leeds and Northrup Model H) coupled to the instrument's output. The columns were run with hydrogen. An Aesculap 40-μl syringe fitted with 20-gauge needle (Record fitting) was used for application of samples. A Riley-Stoker vibrating table.

Reagents

(*a*) *Column:* Tube: $\frac{1}{4}''$ o.d. 18 gauge stainless steel tube (supplied by Messrs. Accles and Pollock in 2-metre lengths). Support: Celite 545 (supplied by Messrs. Johns Manville Ltd.) graded to 40–60 mesh BSS by dry sieving. Static phase: Apiezon M high vacuum grease (prepared by Metropolitan Vickers Electrical Ltd.).

(*b*) *Other reagents:* All of analytical reagent quality except where stated. Methylene chloride, laboratory grade; hydrochloric acid, 500 ml/l; ethyl ether, laboratory grade; sodium bicarbonate; sodium sulphate (anhydrous); methanol (ex I.C.I. redistilled from potassium hydroxide); sulphuric acid 36 *N*; ethyl benzoate solution, 10 g/l, approx. (exactly weighed) in methylene chloride; 4-chloro-2-methyl phenoxyacetic acid (4C2M) (pure, m.p. 120°).

*Preparation of column**

Weigh out 4 g of Apiezon M into a 100-ml beaker and dissolve in 50 ml of chloroform by warming. Add 12 g of Celite 545 and mix thoroughly, adding more chloroform if necessary. Evaporate to dryness on a steam bath and finally heat in an oven at 110° until all trace of solvent has been removed. Stir the powder gently from time to time.

Bend the column (of total length 2 metres) to a U shape and attach a 5-cm funnel to each limb by a short piece of rubber tubing. Apply the bent end of the U to the vibrating table (used at about $\frac{3}{4}$ of its full amplitude) and add $\frac{1}{4}$-g portions of the prepared filling to each leg in turn, allowing a short period for compaction between each addition.

When the funnels fill, turn the vibrator control to full amplitude and hold the column lightly on the surface of the table so that a series of sharp blows is delivered to the bend of the column. Continue this process until no further compaction occurs. Lay the column on the vibrating table occasionally and "bow" across the edge of the table. The whole process takes about 15 min.

Remove the funnels and shake out about 1 cm of the filling from the end of the column. Recompact if necessary. Prepare a piece of glass wool as a rope by rolling between the fingers and folding. Prepare a rope of about 1-cm diameter, cut the end of the rope square with scissors and insert as far as possible into the end of the column. Cut the protruding end square and repeat the process on the other leg.

Form the column to a suitable shape, pull a sleeve of asbestos tube over it and mark with an identity tag.

Column conditions

The column and katharometer block are both operated at 190° with 8 V applied to the detector bridge and a flow rate of 50 ml/min of hydrogen at the output. The input pressure is usually 0.2 kg/cm^2 and the outlet is at atmospheric pressure.

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* These remarks apply particularly to the Perkin Elmer instrument and must be modified to suit the needs of any other instrument.

Calibration

Weigh 1 g of pure 4C2M into a 100-ml flat bottomed flask and add 20 ml of methanol and 1 ml of sulphuric acid. Reflux for one hour. Allow to cool and transfer quantitatively into 100 ml of distilled water. Add solid sodium bicarbonate until evolution of carbon dioxide ceases. Extract with 3 × 10-ml portions of methylene chloride. Wash the combined solvent layers with water. Finally dry the solvent with sodium sulphate, add 10 ml of ethyl benzoate solution from a pipette (*Note*) and evaporate in a hot water bath at 80° just until boiling ceases. Apply 3 µl to the column.

Determination of 4C2M

Weigh out sufficient sample to contain 1–2 g of 4C2M and transfer to a separating funnel, dilute to 50 ml and add, with efficient agitation, sufficient 1 : 1 hydrochloric acid to make distinctly acid. Extract with 3 × 30 ml of ether, combine and wash with 3 × 10-ml portions of distilled water. Discard the aqueous layer after washing it with ether. Evaporate to dryness, add 20 ml of methanol and 1 ml of sulphuric acid and reflux for one hour.

Allow to cool and transfer quantitatively to 100 ml of distilled water in a separating funnel. Add solid sodium bicarbonate until evolution of carbon dioxide ceases. Extract with 3 × 20-ml of methylene chloride. Combine the solvent extracts and wash with 2 × 10-ml of water. Dry the solvent extracts with sodium sulphate and add from a pipette (*Note*) 10 ml of ethyl benzoate solution and evaporate in a hot water bath at 80° until boiling just ceases. Apply 3 µl to the column.

Note

The same pipette should be used for standardisation and determination.

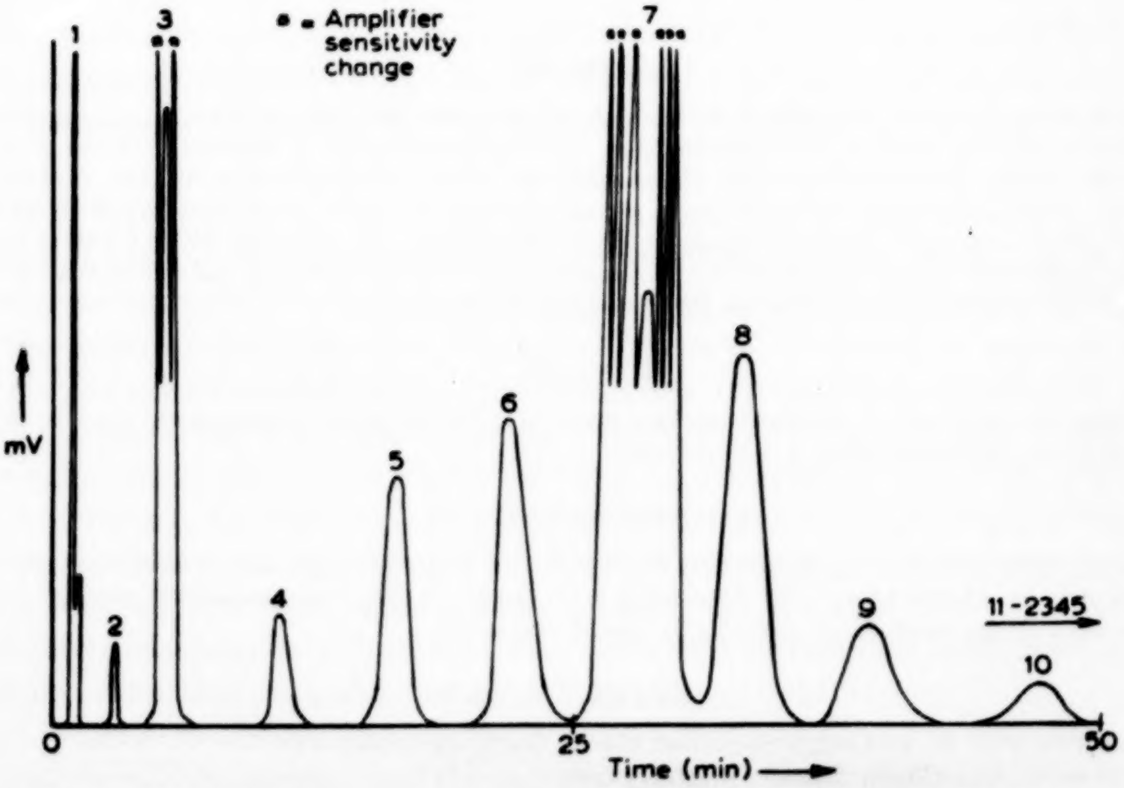

Fig. 1. Amplifier sensitivity change. 1. Solvents from preliminary preparation. 2. Formulant. 3. Internal standard (ethyl benzoate). 4. 2M. 5. Dichlorobenzoic acids. 6. 6C2M. 7. 4C2M. 8. 235 + 245. 9. 234. 10. 46C2M. 11. 2345.

Order of emergence and measurement

The order of emergence is shown in Fig. 1. The method of measurement of area for quantitative determination is that specified by and reported in the Proceedings of the 1st Congress on Gas Chromatography[14]. It has been found necessary to standardise the actual technique of measurement with considerable exactness in order to achieve the confidence limits found. Provided measurement is carried out in exactly the same way in each case, good results will be obtained.

Calculation of results

(*a*) *Calculation of calibration factor.* Determine the areas of the ethyl benzoate and 4C2M (methyl ester) peaks, and calculate as follows. If area of 4C2M peak = a_p; area of ethyl benzoate peak = a_{sc}; weight of pure 4C2M = W_p g; weight of ethyl benzoate taken for calibration = W_{sc} g, and the calibration factor

$$(C) = \frac{W_{sc}\, a_p}{W_p\, a_{sc}}$$

(*b*) *Determination of 4C2M in sample.* Determine the areas of the ethyl benzoate and 4C2M (methyl ester) peaks and calculate as follows. If area of 4C2M (methyl ester) = a; area of ethyl benzoate = a_s; weight of sample taken = W_g g; weight of ethyl benzoate taken for determination = W_s g; 4C2M content of sample

$$= \frac{W_s\, a}{C.W.a_s}\ \%\ \text{w/w}$$

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SUMMARY

A method is proposed for the gas–liquid chromatographic determination of 4-chloro-2-methyl phenoxyacetic acid in MCPA/TBA herbicides. The required acid is separated from associated phenoxacetic acids, chlorocresols and chlorobenzoic acids by conversion to the methyl ester followed by chromatography on a vacuum grease column at 190°. Measurement is by standard addition of ethyl benzoate. Results obtained using admixtures of technical MCPA with TBA show good agreement with those obtained by previously established methods for determination of 4-chloro-2-methyl phenoxyacetic acid in the technical MCPA itself.

RÉSUMÉ

Une méthode chromatographique est décrite pour la séparation et le dosage de l'acide chloro-4-méthyl-2-phénoxyacétique dans des herbicides.

ZUSAMMENFASSUNG

Beschreibung einer chromatographischen Methode zur Bestimmung von 4-Chlor-2-methyl-phenoxyessigsäure in Herbiciden. Die Trennung von anderen Begleitsubstanzen erfolgt auf gaschromatischem Wege nach Überführung in die Methylester.

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DETERMINATION OF FLUORINE IN BERYLLIUM

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One of the processes for producing beryllium involves reduction of beryllium fluoride. It is important, therefore, to know how much fluorine remains in the metal, since large residual amounts of fluorine reduces the already low ductility. Modern vacuum-melting techniques normally reduce the fluorine content to below 0.01% (100 p.p.m.) so that a sensitive method of analysis is required for vacuum-melted material. On the other hand, as much as 0.15% fluorine may be found in 'crude' beryllium metal.

Choice of reagent

There is a wide variety of reagents for determination of trace quantities of fluorine. With one exception (the cerium alizarin complexone reagent described by WEST[1]) these rely on an indirect determination, whereby the colour produced by a metal ion with an organic reagent is inhibited by the fluoride ion which combines preferentially with the metal. Such reagents include the zirconium–eriochrome cyanine lake[2], the zirconium–alizarin S lake[3], the iron–thiocyanate complex[4], the beryllium–chrome azurol S complex[5], the thorium–thoron complex[6], the zirconium–sulphophenylazodihydroxynaphthalene disulphonic acid (SPADNS) complex[7], the aluminium–chromeazurol S complex[8], the thorium–alizarin S lake[9], the thorium–amaranth lake[10], the aluminium–heamatoxylin complex[11], the strontium–chloranilic acid complex[12], the aluminium–eriochromecyanine complex[13], and many others.

There is little to choose in sensitivity between many of these reagents, and the zirconium–SPADNS complex and the cerium–alizarin complexone reagent were chosen for further study, the former because of its marginally greater sensitivity than most of the others, and the latter because it offered a direct determination.

Beryllium interference

It was not considered possible to carry out a determination of fluoride directly on the solution of the metal, because of interference by beryllium itself, and trace impurities in the beryllium. Fluorine was therefore separated by steam distillation. It is known that fluorine is not readily distilled from acid solutions containing beryllium, presumably because of the stability of beryllium fluoride. However, by working at temperatures higher than those normally employed, and using sulphuric acid solutions, a 100% recovery of fluorine could be obtained.

The distillate, besides fluorine, sometimes contained microgram amounts of beryllium, of the order of 10–50 μg. These small quantities may have distilled over, or have been carried over in a fine spray. To avoid a further separation it is therefore desirable that any method for fluorine determination should not be effected by microgram amounts of beryllium.

On investigating the effect of beryllium on the two reagents selected for further study, it was found that even microgram amounts of beryllium seriously interfered with the cerium-alizarin complexone method, as is shown in Table I. Fluorine appeared to complex with the beryllium in preference to the reagent and it would therefore be essential to remove last traces of beryllium if this reagent were to be used.

TABLE I

EFFECT OF Be ON F DETERMINATION BY CERIUM–ALIZARIN COMPLEXONE METHOD

(20 μg F added in each case)

μg Be added	*μg F found*
0	20
5	15
10	11.5
20	8
50	3

Using the zirconium–SPADNS complex, however, the position is considerably more favourable. It will be seen from Table II that there is a small interference — rather surprisingly the beryllium appears to react with the metal complex rather than with the fluoride, so that the interference is positive rather than negative, (but see later under sulphate interference). At the 10-μg level, however, the interference is negligible, and since it is normal to take an aliquot equivalent to 8% of the total distillate, it is most unlikely that there will ever be more than 10 μg Be present in an aliquot.

TABLE II

EFFECT OF Be ON F DETERMINATION BY ZIRCONIUM–SPADNS METHOD

μg Be added	*μg F found (8 μg added)*	*μg F found (nil added)*
0	8.0	0.2
5	8.0	0.2
10	8.1	0.4
20	7.9	1.0
50	8.1	1.5
100	8.5	3.25
200	9.2	4.5

The effect of beryllium on three other possible reagents for fluorine was also investigated. These were the thorium–thoron reagent, the zirconium–alizarin S reagent, and the aluminium–eriochrome cyanine reagent.

Tables III, IV, and V show the extent of the interference. It will be seen that the effect is very similar (interference small) for the three reagents which operate at a fairly high acidity (pH < 1.0), and also similar (large interference) for the two reagents which operate in nearly neutral solution, pH 4–6. This suggests that the stability of the beryllium fluoride complex is much less at high than at low acidities, and confirms our choice of SPADNS as reagent, since of the three used at pH < 1.0 is by far the most sensitive.

TABLE III

EFFECT OF Be ON F DETERMINATION USING THORIUM–THORON REAGENT

μg Be added	*μg F found (10 μg added)*	*μg F found (nil added)*
10	9.8	0.2
20	9.8	0.2
50	10.2	1.0
100	10.5	1.8
200	11.0	4.0

TABLE IV

EFFECT OF Be ON F DETERMINATION USING ZIRCONIUM–ALIZARIN S REAGENT

μg Be added	*μg F found (20 μg added)*	*μg F found (nil added)*
10	20.2	nil
20	20.2	nil
50	20.5	0.4
100	21.0	1.6
200	21.0	3.5

TABLE V

EFFECT OF Be ON F DETERMINATION USING ALUMINIUM–SOLOCHROME CYANINE REAGENT

μg Be added	*μg F found (10 μg F added)*	*μg F found (nil added)*
5	8.0	—1.0
10	6.8	—0.5
20	4.9	—0.5
50	2.5	—0.5

Sulphate interference

Interference of sulphuric acid with the zirconium–SPADNS reagent was also investigated. Table VI shows the extent of interference. It will be noted that it is very similar to that of beryllium. This led us to consider the possibility that the small interference attributed to beryllium in the reagents operating at high acidity was actually due to sulphate, since beryllium sulphate was used in preparing the standard beryllium solution. A further standard beryllium solution was prepared by dissolving

TABLE VI

EFFECT OF SO_4^{-2} ON F DETERMINATION USING ZIRCONIUM–SPADNS REAGENT

μg SO_4^{-2} added	*μg F found (5 μg F added)*	*μg F found (nil added)*	*μg F found (2.5 μg F added)*
50	5.0	nil	2.5
100	5.0	0.2	2.5
200	5.0	0.6	2.65
500	5.1	1.2	2.95
1 mg	5.2	1.6	3.3
2 mg	5.4	2.0	3.8

beryllium metal in hydrochloric acid, and the interference of beryllium studied (Table VII). It will be seen that there is no beryllium interference when present as chloride.

TABLE VII

EFFECT OF Be ($BeCl_2$ SOLUTION) ON F DETERMINATION USING ZIRCONIUM–SPADNS REAGENT

μg Be added	*μg F found (5 μg F added)*	*μg F found (nil added)*
5	5.0	nil
10	5.0	nil
20	5.0	nil
50	4.95	nil
100	4.9	nil
200	4.8	0.1

However, in the distillation procedure adopted, any beryllium passing into the distillate would be present as sulphate, so that interference of beryllium sulphate and sulphuric acid must be considered. It was found that in the procedure adopted, no sulphate could be detected in the distillate. However, it was noticed that in one or two of the initial experiments where the temperature rose to well over 140° (in one case 160°, another 170°) blank determinations were slightly higher than normal, and in fact, a small amount of sulphate was detected in the distillate. By controlling the temperature at 140° carefully, this can be avoided. Various recovery tests were carried out using this procedure. It was necessary to first carry out at least three blank determinations to eliminate traces of fluoride from the steam distillation apparatus used. After three blanks, the blank on 20 ml 20% H_2SO_4 was reduced to 3.3 μg F^- and thereafter remained at this level.

10 ml 40% beryllium sulphate (AnalaR) solution with 20 ml 20% H_2SO_4 was next distilled. A figure of 26 μg F^- was obtained (*i.e.* 22.7 μg F^- from the $BeSO_4$). After the distillation, 25 μg F^- was added to the residue in the distillation flask and the distillation continued. 26 μg F^- were found in the distillate. In a further experiment 25 ml 40% beryllium sulphate solution and 20 ml 20% H_2SO_4 were distilled, and a figure of 60 μg F^- was obtained. (*i.e.* 56.7 μg F^- from the $BeSO_4$). After the distillation 25 μg F^- was added to the residue in the flask and the distillation continued. 28 μg F^- was obtained. (The slighly high recovery is probably due to small amounts of residual F^- after the first distillation).

A similar experiment was carried out with a sample of beryllium metal. Two samples of metal were analysed, and to one 25 μg F^- was added.

The result of the analyses after subtracting the blank, were:

	F^- Found
0.4 g Be	6 μg (= 15 p.p.m. F^-)
0.4 g Be + 25 μg F^-	32 μg
Recovery	26 μg *i.e.* 104%

Those experiments indicate that the distillation procedure is adequate to separate all the fluoride and that there is no interference by the small amount of beryllium or sulphuric acid that comes over with the distillate.

METHOD

Reagents

SPADNS, 0.5 g dissolved in 500 ml water. *Zirconium solution*, dissolve 0.044 g zirconium nitrate in 20 ml conc. HCl and evaporate to dryness. Take up the residue in 200 ml 1 : 1 dilute HCl and dilute to 500 ml. *Reference solution*, to 8 ml SPADNS solution add 1.6 ml conc. HCl and dilute to 100 ml. *Fluoride solution*, take 5 ml standard fluoride solution (500 p.p.m.) and dilute to 500 ml. 1 ml = 5 μg F (Store in polythene).

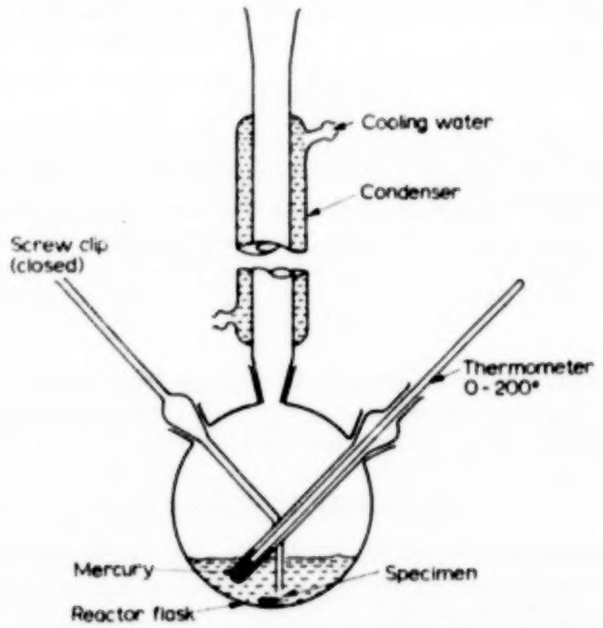
Cooling water
Condenser
Screw clip (closed)
Thermometer 0-200°
Mercury
Specimen
Reactor flask

Fig. 1. Arrangement of apparatus for digesting sample.

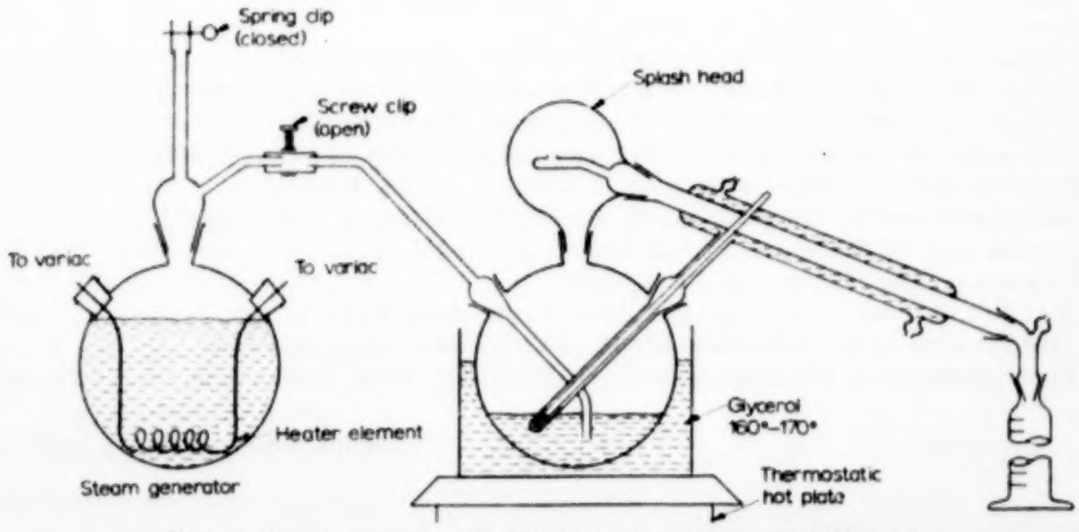
Spring clip (closed)
Splash head
Screw clip (open)
To variac
To variac
Heater element
Steam generator
Glycerol 160°–170°
Thermostatic hot plate

Fig. 2. Arrangement of apparatus for steam distillation.

Calibration

Take 0, 1, 2, 3, 4, 5, 0.2, 0.5, 0.8, 1.5 ml of standard F^- solution, dilute to about 20 ml, add 2 ml Zr solution and 2 ml SPADNS solution (both by pipette). Dilute to 25 ml and leave for 5 min. Measure the absorption against the reference solution at 5900 Å, 4-cm cells.

Procedure

Dissolve about 0.4 g Be (catch-weight, weighed accurately) in 55 ml 20% dilute H_2SO_4 in a distillation flask fitted with a reflux condenser, a thermometer, and a tube for steam distillation (clipped off at this stage), (Fig. 1). When the metal has dissolved, replace the reflux condenser with a splash head and an ordinary condenser for distillation, place a graduated receiver for the distillate, immerse the distillation flask in a glycerol bath at 160°–170° (Fig. 2) and distil until the temperature of the solution is 125°. At this point release the clip on the steam tube, and steam distil, collecting 2 × 125-ml portions of distillate. (The temperature should rise to about 140° about half way through the distillation, and remain at this temperature). Treat each distillate separately, taking a 20-ml aliquot and treating it as under 'calibration'. The F^- content of the second distillate should not be more than $\frac{1}{4}$ of that in the first distillate. If it is, distil a further 125 ml. Calculate the total fluoride content of the distillate, do a blank determination in a similar manner, and thence obtain the fluoride content of the sample. A single determination takes about three hours.

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SUMMARY

Various reagents for the determination of fluorine in beryllium have been investigated and a method is described using the zirconium sulphophenylazodihydroxynaphthalene disulphonic acid (SPADNS) complex. The fluoride is steam distilled from a sulphuric acid solution, under carefully controlled conditions, and aliquots of the distillate are treated with the reagent and measured spectrophotometrically at 5900 Å. Interference by beryllium and by sulphate ions is discussed.

RÉSUMÉ

Plusieurs réactifs ont été examinés en vue du dosage du fluor dans le béryllium. Une méthode spectrophotométrique est décrite, utilisant l'acide sulfophénylazodihydroxynaphtalène disulfonique. Le fluor doit être séparé au préalable par distillation.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Fluor in Beryllium mit Hilfe des Zirkoniumskomplexes der Sulfophenyl-azo-dihydroxynaphthalin-disulfosäure nach Abtrennung des Fluors durch Destillation.

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A REINVESTIGATION OF THE DETERMINATION OF THORIUM WITH SPADNS

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INTRODUCTION

A method was required for the determination of low concentrations of thorium in the accessory minerals of igneous rocks. As these are often available only in limited quantities, high sensitivity was essential.

A report by BANERJEE[1] on the use of SPADNS [2-(*p*-sulphophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid] as a colorimetric reagent in the spectrophotometric determination of thorium, claimed the method to be capable of estimating quantities as low as 0.04 μg. The apparent superiority of this reagent in the microgram range compared with APANS[2,3], arsenazo[4], morin[5] and others[6-8], suggested its use in the final determination of thorium after separation of associated interfering elements.

Preliminary tests, however, showed that a measurable intensity of the blue-violet thorium–SPADNS complex could only be achieved at thorium concentrations greatly in excess of the figure reported. Also, the use of acetate buffer solutions, as mentioned by BANERJEE, was found to reduce colour intensity.

Despite these inconsistencies the method still appeared adaptable to the above problem and a reinvestigation of all the factors pertinent to the determination was considered desirable.

EXPERIMENTAL

Reagents

Pure SPADNS reagent (Na salt) was synthesised according to the technique described[9] and a 0.1% aqueous solution prepared. A thorium solution was made by dissolving approximately 6.0 g of AnalaR thorium nitrate tetrahydrate in distilled water and diluting to 250 ml. This was standardised by igniting 5-ml aliquots to thorium oxide and weighing after attaining constant weight. Two successive dilutions of 10 : 1000 and 10 : 100 respectively yielded a standard solution containing 9.75 μg thorium per ml (Solution A). At this level it was found essential to prepare fresh dilutions before use.

Apparatus

A Unicam S.P. 500 spectrophotometer and 1-cm cells were employed for absorption measurements, all solutions being diluted to a final volume of 25 ml before measurement. Acidities were adjusted using a Jones pH meter.

Wavelength and pH

A check on the optimum wavelength for measurement of the blue-violet complex and the desirable acidity for colour development gave results similar to those reported in the original paper: *viz.*, maximum absorption at 580 mμ and colorimetric stability at acidities between pH 2.6 and pH 3.6. A pH of 3.1 was chosen as the desirable acidity for colour development; this was equivalent to 3.5 ml 0.01 *N* HCl in 25 ml of the final solution.

The maxima and minima of the wavelength–optical density curves for SPADNS and thorium–SPADNS against water as a reference coincided exactly with those shown by BANERJEE, thus confirming the correct identity of the SPADNS reagent prepared for this investigation.

Effect of varying the amount of reagent

To a number of aliquots of solution containing 97.5 μg thorium as a working concentration, varying amounts of 0.1% SPADNS reagent were added. After acidity adjustment, volumes were made up to 25 ml and optical densities measured against reference solutions, similarly adjusted and containing corresponding amounts of the reagent.

From the plot of the results 1 ml of colour reagent was found to be sufficient for the range of 0–100 μg thorium. This curve differs from that of BANERJEE, as shown in Fig. 1.

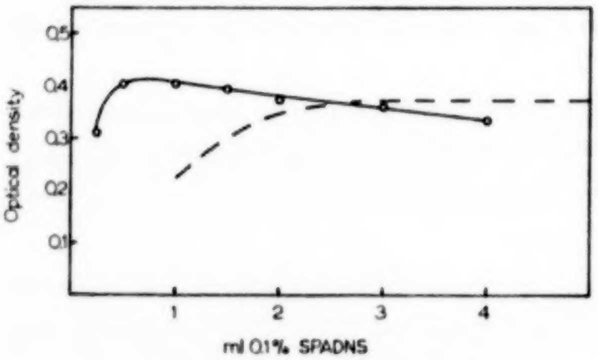

Fig. 1. Effect of reagent.
———— This work – 100 μg Th
- - - - - - - - BANERJEE – 4 μg Th

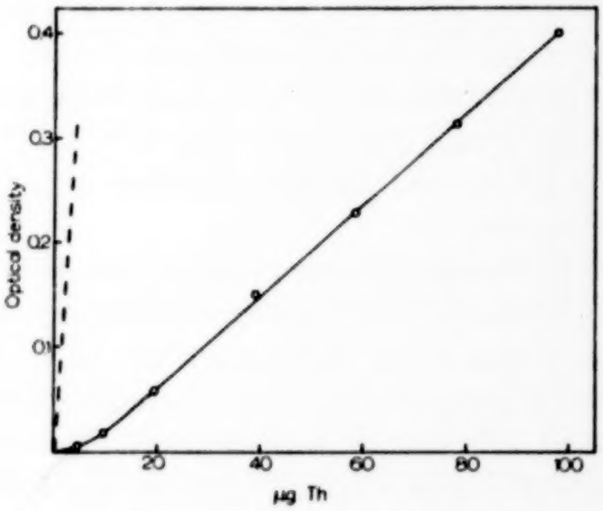

Fig. 2. Calibration curve.
———— This work
- - - - - - - - BANERJEE

Effect of time on colour intensity

All solutions were left for one hour for maximum colour to develop and remained stable for at least 24 h.

Calibration

0.5- to 10-ml aliquots of freshly prepared solution A containing 4.88 to 97.5 μg of thorium were made up to a volume of 25 ml with distilled water after the addition of 0.1% SPADNS reagent and 3.5 ml 0.01 *N* HCl. After standing for 1 h optical densities were measured against a reference solution containing reagents at a wavelength of 580 mμ. The optical density–concentration curve is shown in Fig. 2. Below 10 μg thorium, a deflection of the curve through the origin was apparent.

Molecular ratio of combination

The molecular ratio of thorium–SPADNS combination was confirmed as being 1 : 1 by the slope–ratio method. The actual figure obtained was 0.97 : 1.

Effect of acetate ions

Visual tests indicated that the presence of acetate ions had a marked effect on the blue-violet colour of the thorium complex, small amounts decreasing the intensity and larger amounts removing it entirely.

A series of thorium–SPADNS standards each containing 97.5 µg thorium and 1.0 ml of reagent was buffered with increasing volumes of a sodium acetate–HCl buffer (pH 3.1) of known acetate content. The optical densities, measured and plotted against acetate content (Fig. 3) showed that the intensity of colour of the thorium complex decreased rapidly until it disappeared entirely, leaving the original SPADNS colour.

A second series of standards increasing in thorium content up to 1600 µg/25 ml of solution but containing identical amounts of sodium acetate–HCl buffer (equivalent to 250 mg sodium acetate) and 1 ml of 0.1% SPADNS, was then measured. A straight line graph (Fig. 4) showing greatly reduced sensitivity (Sandell's definition, 0.3 µg·cm^{-2})[10] was obtained.

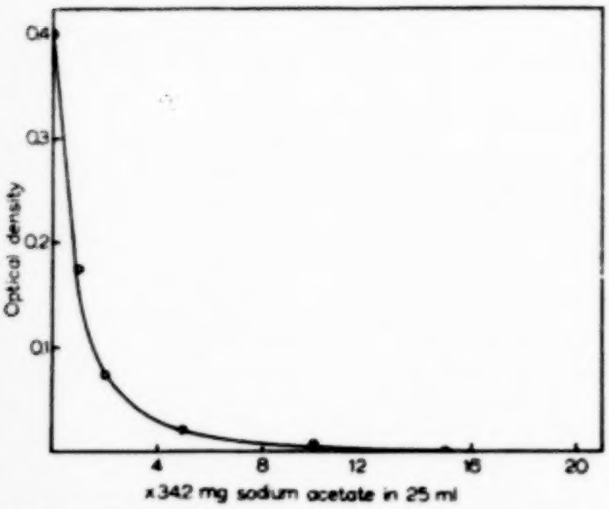

Fig. 3. Effect of increasing acetate content.

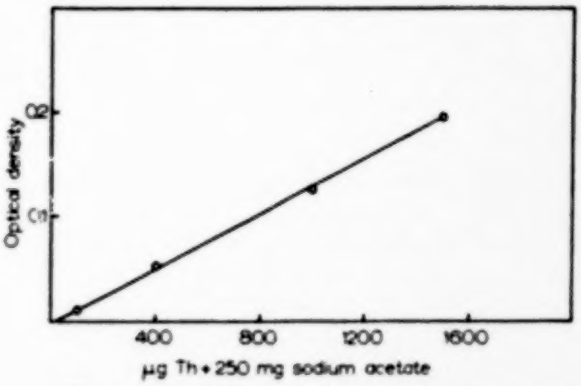

Fig. 4. Calibration curve in presence of acetate (equivalent to 250 mg sodium acetate).

DISCUSSION

A comparison of this work with that previously reported by BANERJEE has shown several major differences. Present investigations have established that 1 ml of 0.1% SPADNS is required to complex 100 µg thorium (Fig. 1). A molar combination ratio 1 : 1 shows this to be a four-fold excess, a figure in marked contrast to a 300-times excess arising from BANERJEE's use of 3 ml of 0.1% SPADNS reagent for 4 µg thorium.

BANERJEE also states that the lower practical limit of determination is 0.04 µg thorium, but examination of his graph shows this to be impracticable. The present work indicates 10 µg thorium to be the lower limit for practical use.

According to Sandell's definition[10], the sensitivity of the colour reaction between SPADNS and thorium derived from the calibration graph (Fig. 2), is 0.011 µg Th cm^{-2}

for log $I_0/I = 0.001$ at 580 mμ. BANERJEE reports a comparable figure, *viz.* 0.012 μg Th cm^{-2}, which is not in accord with his results. The recalculated value, 0.00048 μg Th cm^{-2}, which is based on his stated optical density measurement of 0.334 for 4 μg thorium in 25 ml solution, is improbable.

The present work shows that the method is comparable with other procedures, the sensitivity of the SPADNS reagent being between that of APANS (0.015 μg Th cm^{-2}) and morin (0.007 μg Th cm^{-2}).

ACKNOWLEDGEMENTS

This work was undertaken to investigate the problem of thorium determination in rock matrices and accessory minerals. It was carried out as part of a geological age programme on Australian rocks. It was initiated by Mr. H. BERRY, to whom acknowledgement is gratefully made.

SUMMARY

A reinvestigation is reported of the spectrophotometric micro-determination of thorium with SPADNS, 2-*p*-sulphophenylazo-1,8-dihydroxy-naphthalene-3,6-disulphonic acid. It is shown that the practical lower limit of determination is 10 μg against a previously reported value of 0.04 μg. Increasing macro-quantities of acetate are shown to reduce the developed colour finally removing it. The molecular ratio of combination of thorium–SPADNS is confirmed as being 1 : 1.

RÉSUMÉ

Une nouvelle étude a été effectuée à propos du microdosage spectrophotométrique du thorium, au moyen de l'acide (*p*-sulfophénylazo)-2-dihydroxy-1,8-naphtalène disulfonique-3,6 (SPADNS).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die spektrophotometrische Mikrobestimmung von Thorium mit Hilfe von SPADNS (2-*p*-sulfophenylazo)-1,8-dihydroxynaphtalin-3,6-disulfosäure).

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THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM AS MOLYBDOVANADIC ACID

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INTRODUCTION

Many of the most sensitive spectrophotometric methods for vanadium are based upon mixed heteropoly acids containing this element or upon their reduction products. The procedure based upon tungstovanadophosphoric acid[1] has been accepted for many years. Methods based on molybdovanadophosphoric acid have also been proposed[2,3].

Although simple heteropoly acids of vanadium have been known for many years, their application to analytical chemistry has not been explored. A search of the literature revealed only two instances where the use of simple molybdovanadic acids is mentioned. DECKERT[4] employed a simple molybdovanadic acid to precipitate morphine and assigned the formula $C_{17}H_{19}NO_3 \cdot 2MoO_3 \cdot V(OH)_5$ to the precipitate. WOODMAN AND CAYVAN[5] noted that, under certain conditions, a yellow hue developed as a result of interaction between molybdic and vanadic acids. Although they stated that as little as 10^{-6} g of vanadium per 50 ml could be detected, they actually did little experimental work and some of their statements were found to be erroneous. GULLSTROM[6] initiated a study of this system.

This paper presents the results of a study to determine the analytical applications of the molybdovanadic acid system to the determination of vanadium.

EXPERIMENTAL

Apparatus

All photometric measurements were made on a Cary recording spectrophotometer, Model 10–11. The optical path length of the fused quartz absorption cells was 1.000 ± 0.002 cm. A Leeds and Northrup glass electrode pH meter was used for pH measurements. The meter was standardized before each series of measurements with commercially available buffers. Microburets were used for dispensing definite, small volumes of reagents.

Reagents

A stock solution of sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, was prepared by dissolving 20 g in 500 ml of distilled water and diluting to the graduation mark in a 1000-ml volumetric flask. The vanadium pentoxide was purified by the procedure of WRIGHT AND MELLON[1]. A solution containing approximately 0.1 g of vanadium per ml was prepared by dissolving 0.1785 g of the purified vanadium pentoxide in 300 ml of approximately 0.1 N sodium hydroxide, acidifying with sulfuric acid to a pH of about 6.0, diluting to the graduation mark in a 1000-ml volumetric flask, and mixing. The solution was standardized by the method of WILLARD AND YOUNG[7].

The color reaction

The intense yellow hue of a solution containing molybdic and vanadic acids, at an appropriate pH, is almost certainly due to the formation of a simple heteropoly acid composed of these acids. The isolation of various molybdovanadic acids and their salts by a number of workers[8-10] leaves little doubt of the existence of such complexes.

While the existence of these heteropoly acids is well-substantiated, the structures and formulations have been the subject of considerable controversy. ROSENHEIM[11] and others[12,13] list vanadium with the elements which are capable of functioning as central atoms. That it actually is doing so in the various complexes isolated has never been shown.

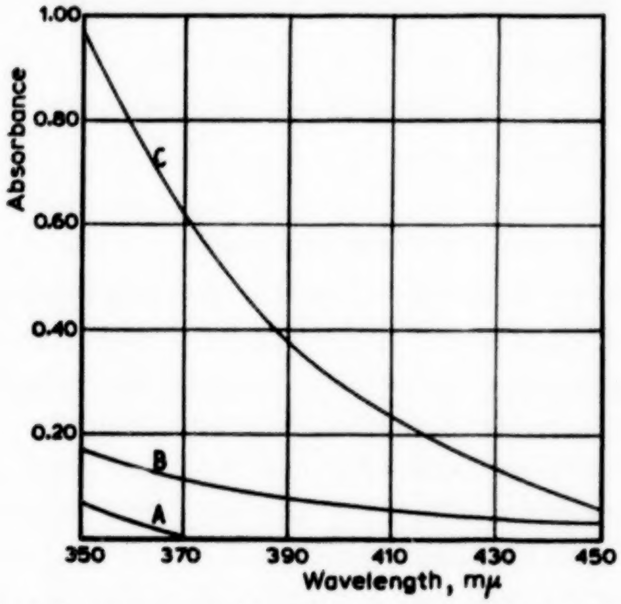

Fig. 1. Absorption spectra of A: vanadic acid, B: molybdic acid, and C: 5-molybdovanadic acid.

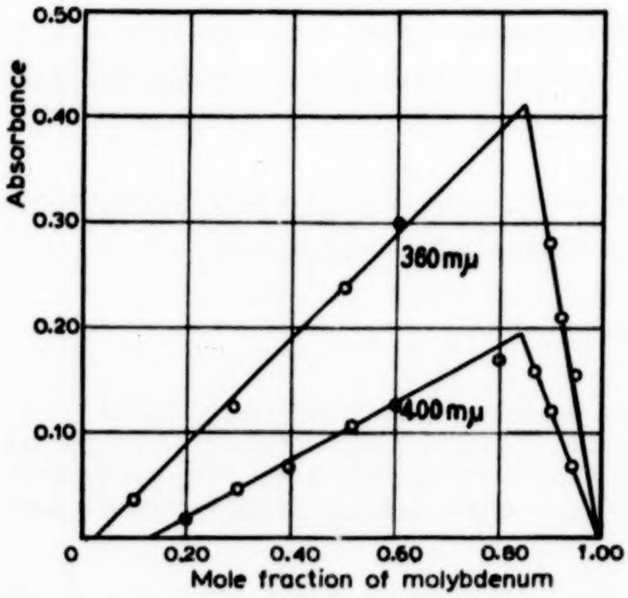

Fig. 2. Determination of ratio of molybdenum to vanadium by method of continuous variations.

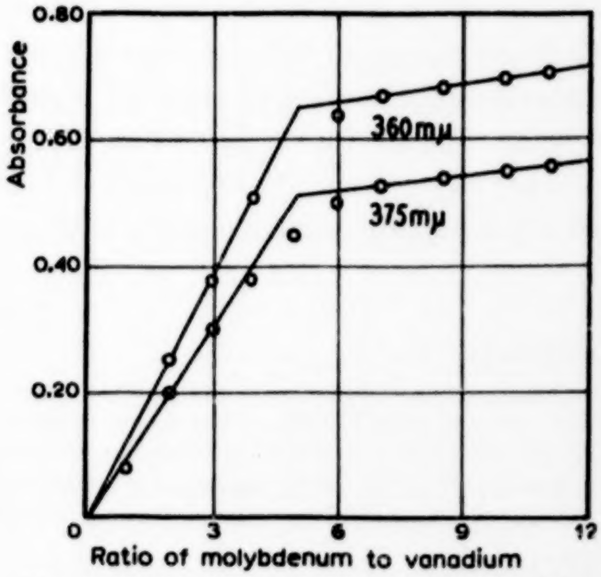

Fig. 3. Determination of ratio of molybdenum to vanadium by mole ratio method.

1. *Nature of the reaction.* Evidence that molybdic and vanadic acids interact is given in Fig. 1. The absorption spectra of A, vanadic acid at pH 3.0 (0.5 mg V/50 ml), of B, molybdic acid at pH 3.0 (5 ml of 2% Na_2MoO_4/50 ml), and of C, a mixture of vanadic and molybdic acids at the same concentrations are shown. The large deviation of the absorption spectrum of the mixture from that expected from a simple additivity of the absorption spectra of the constituents, indicates a major change in the nature of the absorbing species. This change is attributed to heteropoly acid formation. Also the hue of the solution changed.

A spectrophotometric study of the composition of the complex formed was undertaken. Both the method of continuous variations[14] and the mole ratio method[15] were employed. The results of both methods (Figs. 2 and 3) indicate that a complex containing a molybdenum to vanadium ratio of 5 to 1 is formed under the condition studied.

It is to be expected that the properties of this 5 to 1 complex would be considerably different from the properties of the heteropoly acids of the saturated or 12-series. Although the 5 to 1 complex was reducible using 1-amino-2-naphthol-4-sulfonic acid as a reductant, prepared as directed by FABER[16], the product was purple, not the heteropoly blue obtained with the 12-series. In addition, the intensity of the purple hue for a given concentration of vanadium was much less than the intensity of the unreduced complex, unlike the 12-series where reduction increases the sensitivity. Thus, no analytical advantage would be gained by reduction.

2. *Effect of variables.* Studies were made of the variables likely to affect the color reaction.

(*a*) *Acidity.* The effect of acidity on the formation of 5-molybdovanadic acid is very marked. The acid is stable only over a very narrow pH range, as shown in Fig. 4. The optimum acidity for maximum color development is from pH 3.0 to 3.5. Deviation from this range results in decomposition or incomplete formation of the complex. The optimum acidity is independent of both the molybdate and vanadate concentration. It is also independent of the acid used. Various mineral acids, such as sulfuric, nitric, perchloric, and hydrochloric, gave identical results.

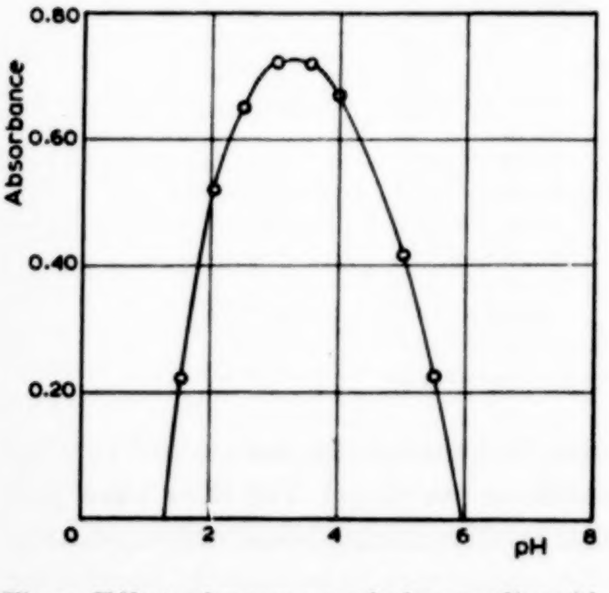

Fig. 4. Effect of pH on 5-molydovanadic acid.

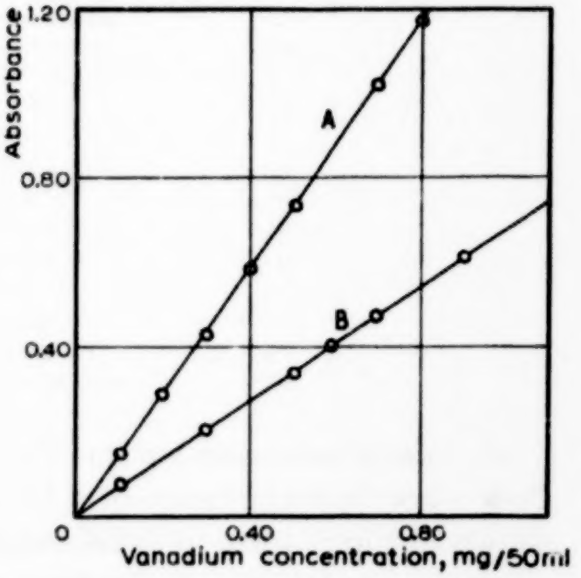

Fig. 5. Beer's law plot for A: 5-molybdovanadic acid, and B: tungstovanadophosphoric acid.

(*b*) *Time.* The complex acid is stable for at least 24 h. However, contamination with silica must be avoided by storing the solutions in polyethylene if measurements are delayed. If this is not done, 12-molybdosilicic acid is formed which also absorbs radiant energy in the same spectral region as 5-molybdovanadic acid.

The complete formation of the 5-molybdovanadic acid requires a period of 20 to 30 min, as determined by following the absorbance as a function of time, at a wavelength of 360 mμ.

The data obtained by this study are shown in Table I.

TABLE I

EFFECT OF TIME ON THE 5-MOLYBDOVANADIC ACID SYSTEM

Time *min*	*Absorbance* *360 mμ*
1	0.59
3	0.68
5	0.73
10	0.75
20	0.76
30	0.77
60	0.77
24 h	0.77

(*c*) *Molybdate concentration.* All reactions which result in heteropoly acid formation are equilibrium reactions. This being the case, an excess of the coordinating anhydride is required in order to shift the reaction toward practically complete formation of the complex acid. For the 5-molybdovanadic acid, an excess of molybdate over the stoichiometric amount calculated for a 5 to 1 ratio was necessary for complete color development (See Table II).

TABLE II

EFFECT OF MOLYBDATE CONCENTRATION

Volume of 2% sodium molybdate *ml*	*Absorbance* *(375 mμ)*
0	0.00
0.5	0.56
1.0	0.66
2.0	0.68
3.0	0.69
4.0	0.70
5.0	0.70
10.0	0.70
15.0	0.71

(*d*) *Vanadium concentration.* The 5-molybdovanadic acid system was found to obey Beer's law over the range of 0 to 1.5 mg of vanadium per 50 ml. The Beer's law plot shown in Fig. 5 for 5-molybdovanadic acid and tungstovanadophosphoric acid compares the sensitivities of the two systems.

(*e*) *Diverse ions.* In order to determine the limitations of an analytical method based on 5-molybdovanadic acid imposed by the matrix material, a study of the effect of selected diverse ions was made. The results of this study are summarized in Table III.

The ions Na^+, Cu^{+2}, Cd^{+2}, Zn^{+2}, BO_3^{-3}, Cl^-, NO_3^-, SO_4^{-2}, ClO_4^-, Br^-, and I^- were found to exert no influence up to at least 200 times the vanadium concentration on a weight/weight basis. One effect should be noted, however. If Br^- and I^- ions are present in the sample, the absorbance must be measured within 45 min after the addition of the sodium molybdate. If this is not done, the error of the vanadium determination will be greater than 2%. The absorbance of solutions containing Br^- and I^- increases greatly with time.

TABLE III

EFFECT OF DIVERSE IONS ON 5-MOLYBDOVANADIC ACID

The absorbance of 5-molybdovanadic acid alone was 0.740

Ion	*Added as*	*Amount added mg/50 ml*	*Absorbance 360 mμ*	*Amount permissible mg/50 ml*
Al^{+3}	$Al(NO_3)_3$	100	0.700	50
AsO_4^{-3}	NaH_2AsO_4	10	0.545	0
BO_3^{-3}	H_3BO_3	100	0.740	100
Ba^{+2}	$Ba(NO_3)_2$	100	*	0
Bi^{+3}	$Bi(NO_3)_3$	100	*	0
Br^-	NaBr	100	0.740	100
Cd^{+2}	$Cd(NO_3)_2$	100	0.730	100
Citrate	$Na_3C_6H_5O_7$	100	0.07	0
Cl^-	NaCl	100	0.740	100
ClO_4^-	$HClO_4$	100	0.740	100
Co^{+2}	$Co(NO_3)_2$	75	0.725	75
$Cr_2O_7^{-2}$	$K_2Cr_2O_7$	1	1.170	0
Cu^{+2}	$CuSO_4$	100	0.730	100
Fe^{+3}	$FeCl_3$	100	*	0
GeO_4^{-2}	H_2GeO_4	5	2.00	1
I^-	NaI	100	0.750	100
K^+	KCl	100	0.60	5
Mg^{+2}	$MgSO_4$	100	0.720	85
Mn^{+2}	$MnSO_4$	75	0.725	75
NH_4^+	NH_4Cl	100	0.585	5
NO_3^-	$NaNO_3$	100	0.740	100
Na^+	NaCl	100	0.740	100
Ni^{+2}	$NiCl_2$	100	0.840	25
Oxalate	$Na_2C_2O_4$	100	0.04	0
PO_4^{-3}	KH_2PO_4	50	0.785	20
Pb^{+2}	$Pb(NO_3)_2$	100	*	0
SO_4^{-2}	Na_2SO_4	100	0.730	100
SiO_3^{-2}	Na_2SiO_3	1	2.00	0
Tartrate	$Na_2C_4H_4O_6$	100	0.06	0
WO_4^{-2}	Na_2WO_4	100	1.42	30
Zn^{+2}	$Zn(NO_3)_2$	100	0.730	100

* Precipitate produced

Many other ions, such as Mn^{+2}, Co^{+2}, Ni^{+2}, Mg^{+2}, WO_4^{-2}, Al^{+3}, and PO_4^{-3}, can be present in smaller amounts but in large enough concentrations that little difficulty would be encountered with most samples.

A serious source of interference results from precipitation of heavy metal salts of molybdic acid at the operating pH. The ions tested which interfere in this manner are Ba^{+2}, Pb^{+2}, Bi^{+3} and Fe^{+3}. The interference of iron in this manner can be eliminated by lowering the pH and adding fluoride ion. Unfortunately, if this is done, the sensitivity is lowered to the point where other methods become preferable, thus necessitating the removal of iron.

Another class of ions causing major interference are those capable of condensing with molybdic acid, such as SiO_3^{-2}, GeO_4^{-2}, and AsO_4^{-3}, to yield heteropoly acids. The interference of these ions was to be expected. Fortunately, they are separated relatively easily from vanadium when necessary. It is interesting to note that the phosphate ion, PO_4^{-3}, can be tolerated in amounts up to 20 mg per 50 ml. This is undoubtedly due to the difference in the stability of the 12-heteropoly acids of phosphorous and silicon to pH changes. Silicon forms stable complexes at relatively high pH values while the 12-heteropoly acid containing the phosphorus as the central atom begins degradation to colorless usaturated heteropoly acids at a much lower pH.

RECOMMENDED GENERAL PROCEDURE

Preparation of the calibration curve

Add to a series of 100-ml polyethylene beakers, 0, 0.5, 1.0, 5.0, and 10 ml of a standard solution of sodium vanadate containing 0.1 mg of vanadium per 50 ml. To each beaker add 10 ml of water and 10 ml of 2% sodium molybdate. Adjust to pH 3.0 ± 0.1. Allow the solutions to stand for 30 min and measure the absorbance at 360 mμ. Plot the absorbances *versus* the corresponding concentrations of vanadium.

Procedure

Select and dissolve, if necessary, the sample in which vanadium is to be determined. Treat the resulting solution to remove or complex the interfering ions according to standard methods. Concentrate the solution to a volume not exceeding 25 ml and add 10 ml of two per cent sodium molybdate. Adjust the acidity of the solution carefully to pH 3.0 ± 0.1 and transfer it to a 50-ml volumetric flask. Dilute to the graduation mark, mix, and allow to stand for 30 min. Measure the absorbance of the solution at 360 mμ and compare with a calibration curve prepared as directed. As the absorbance measurement is made on a rather steep slope, care must be taken to maintain reproducible wavelength settings.

PROCEDURE FOR VANADIUM IN STEELS

The elemental composition of vanadium-bearing steels most often includes the elements Mn, Cr, Si, P, Cu, C, S, W, and Fe in addition to vanadium. Of these elements, it will be necessary to remove Fe, Cr, and Si. The other elements either do not interfere or are normally present in such concentrations that they will not interfere. The procedure proposed yielded reliable results on three such steel samples obtained from the National Bureau of Standards.

Procedure

Weigh out a sample of steel that contains from 0.01 to 1.0 mg of vanadium. Larger samples will require that an aliquot be taken for the final measurement. Add to the sample in a tall, covered beaker 15 ml of hydrochloric acid (2 : 1). Cover and warm gently until all action ceases. Remove the cover, after rinsing, and cautiously add nitric acid (1 : 1) dropwise until the vigorous evolution of nitric oxide ceases. Add 50 ml more, replace the cover, and heat to boiling, gently at first, and then strongly until all black particles have disappeared.

If tungsten is present, it must be filtered off before proceeding with the next step. Dilute the solution to about 50 ml and filter off the silica and hydrated tungstic oxide. Wash with (2 : 1) hydrochloric acid and then concentrate the filtrate and the wash solutions to a volume of 15 ml. If tungsten is not present, the solution resulting from the sample dissolution may be concentrated directly.

Transfer the solution to a 250-ml separatory funnel and rinse the beaker with (2 : 1) hydrochloric acid. The total volume of the solution should not greatly exceed 25 ml. Cool the solution and extract the iron with dichlorodiethyl ether. With this extractant the acidity need not be controlled as closely as with diethylether and repeated extractions may be made without transferring the aqueous layer since dichlorodiethyl ether is more dense than water. After removal of the iron, rinse the contents of the separatory funnel into a tall beaker. Warm the solution to remove the ether, and add nitric acid to oxidize any remaining organic material on heating to boiling. Cool, add 50 ml of 70% perchloric acid, and evaporate to fuming. Cool again and dilute to 30 ml. Add a molar solution of lead nitrate dropwise as long as a precipitate of lead chromate forms. Addition of a few drops of dilute sulfuric acid will precipitate the excess lead.

Filter off the combined precipitates of lead chromate, lead sulfate, and silica. Concentrate the filtrate to 25 ml and proceed as directed under the general procedure.

The above procedure for the separation of interfering ions and the general color development procedure were tested on three steel samples obtained from the National Bureau of Standards. The results of analyses of these samples employing the procedures described are given in Table IV. The procedure yields precise and accurate results.

TABLE IV

ANALYSES OF NBS STEELS FOR VANADIUM

NBS Steel No.	*Percentage of V*		*Relative error of av.* %	*Standard deviation* %
	Certified	*Found (av.)*		
30^{e}	0.235	0.239[a]	1.70	0.005
50^{a}	0.970	0.969[b]	0.10	0.008
153	2.04	2.09[c]	2.45	0.056

[a] Four determinations.
[b] Six determinations.
[c] Five determinations.

DISCUSSION AND CONCLUSIONS

A spectrophotometric method for vanadium based on the yellow hue of 5-molybdovanadic acid yields reliable results. It is more sensitive than the standard tungstovanadophosphoric acid method, with about the same interferences.

The method is subject to a number of disadvantages, principally the interference of iron and chromium. Where high sensitivity and accuracy are required, however, the removal of these interfering ions can be accomplished. A minor defect is the rather close regulation of pH that is required.

Reduction of the 5-molybdovanadic acid to molybdenum blue is possible, but the product has weak absorption. This step appeared to offer no advantages as a basis for an analytical method.

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support of this work through fellowship grants by the United States Rubber Company and the Union Carbide Chemicals Company.

SUMMARY

A colored complex formed by the condensation of the oxy-acids of molybdenum(VI) and vanadium(V) in a 5 to 1 ratio is used as the basis for a spectrophotometric method for vanadium. The absorbance of the intense yellow complex is measured at 360 mμ. The color is stable for at least 24 h and follows Beer's law over the concentration range of $2 \cdot 10^{-5}$ to $6 \cdot 10^{-4}$ M vanadium. A standard deviation of 0.056% in steel samples containing 2.04% vanadium was obtained for five determinations. Factors affecting the color formation and the analytical applications to the determination of vanadium are presented.

RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique du vanadium, sous forme d'acide molybdovanadique. On décrit également un procédé pour le dosage de cet élément dans les aciers.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Vanadium in Form der Molybdo-vanadinsäure und deren Anwendung zur Bestimmung von Vanadium in Stahl.

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THE DETERMINATION OF FREE ACID IN PLUTONIUM SOLUTIONS*

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INTRODUCTION

The determination of the free acid in plutonium process solutions requires a method that will prevent interference from hydrolysis of the plutonium ions. There are many references in the literature to procedures for the determination of free acid in the presence of hydrolyzable ions. These procedures either remove the hydrolyzable ions before titration of the free acid or correct for the effect of the hydrolysis of the ions on the free acid result. These procedures can be divided into three general methods. The first of these methods involves dilution of the sample to an appropriate acid concentration range and then the use of pH as a measure of the free acid content[1,2]. The second of the methods involves precipitation and removal of the hydrolyzable ions and then the determination of the free acid remaining in the solution in a conventional manner[3-5]. The third method, which is more generally applicable, involves the formation of a soluble complex of the hydrolyzable ions and then the titration of the free acid in the presence of this complex[6-8]. A procedure based on this third method has been used in this laboratory for the determination of free acid in the presence of plutonium, but results have at times been inconsistent. So an investigation of the method was undertaken and the results are presented in this paper.

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* Work done under AEC Contract AT(29-1)-1106.

REAGENT AND APPARATUS

Complexing solutions: 10% (w/v) solutions of reagent grade sodium citrate, potassium oxalate and potassium tartrate; plutonium sulfate: prepared by precipitation from a plutonium(IV) nitrate solution; standard solutions of HNO_3 and NaOH; Precision-Dow titrator: a recording titrator manufactured by the Precision Scientific Company.

PROCEDURE

The Precision-Dow titrator was used for all the titrations. In the bias determination study, a 30-ml portion of the complexing agent being investigated was placed in a beaker and the pH adjusted to the desired value using either NaOH or a saturated solution of an appropriate acid (citric, oxalic or tartaric, depending on the complexing solution being investigated). Then 26 mg of $Pu(SO_4)_2$ was added (this quantity is equivalent to the amount of Pu in the samples usually taken for a free acid determination), dissolved, and the pH redetermined. The desired quantity of standard HNO_3, representing the free acid, was then added and the solution titrated with standard NaOH. The redetermined pH of the solution after the plutonium had been added was taken as the pH for determining the end-point of the titration. This procedure corrected for the residual acid in the plutonium sulfate.

For titrations in which nitric acid solutions of plutonium were used as the source of plutonium, the procedure was the same as described above except that the pH of the complexing solution before the addition of the plutonium was used as the pH for determining the end-point.

DISCUSSION

The procedure that has been used in this laboratory for determining free acid in solutions containing plutonium involves addition of potassium oxalate to the samples, then titration with a standard base to the methyl red end-point. The primary difficulty with this procedure is in finding the end-point. At the pH at which methyl red changes color, the titration curve is rather flat. Even with oxalate present, plutonium hydroxide begins to precipitate near the end-point, making the solution quite cloudy. The solution is also brown from plutonium(IV) making the color change of the indicator very difficult to determine.

To eliminate this difficulty with the visual end-point detection, a potentiometric end-point procedure, using a glass and a calomel electrode, was substituted for the methyl red indicator. The titration curves were recorded with a Precision-Dow titrator.

Using the potentiometric end-point procedure, potassium oxalate, sodium citrate and potassium tartrate were investigated as complexing agents. (Potassium fluoride, another possible complexing agent, was not investigated because of known precipitate formation with resulting recovery difficulties). An insoluble precipitate was obtained using potassium tartrate. Using the oxalate, a plutonium hydroxide precipitate began to form at a pH of about 4. With the citrate, no precipitate was formed even at a pH as high as 11. Both the oxalate and the citrate were investigated more thoroughly.

Investigation of bias

In the determination of free acid in the presence of hydrolyzable ions by titration with base, there is the possibility of a bias being introduced by the reaction of hydroxyl ions with the hydrolyzable ions. If this bias is large, the results obtained are obviously useless. It is necessary, therefore, in any proposed procedure to determine if there is a bias, and if there is, its size.

The presence of a bias can be determined by adding a complexing agent and a known amount of acid to a solution containing hydrolyzable ions, then titrating the acid and calculating the recovery[8]. Since the complexing agent is usually a salt of a weak organic acid, the concentration of the anion available for complexing the hydrolyzable ion is governed by the pH of the solution. Therefore, the titration is carried out over a range of pH values and the difference between the calculated normality of the acid and the known normality of acid added is determined. This difference is plotted *versus* the pH of the solution in which the titration is performed. From this plot it is possible to determine the pH at which there is a minimum bias. In subsequent

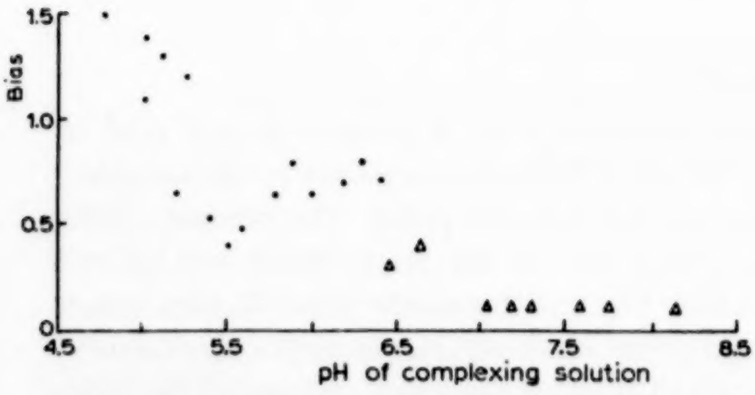

Fig. 1. Bias curve. Complexing solutions, △ = 10% sodium citrate; ● = 10% potassium oxalate. Bias, normality calculated minus normality known.

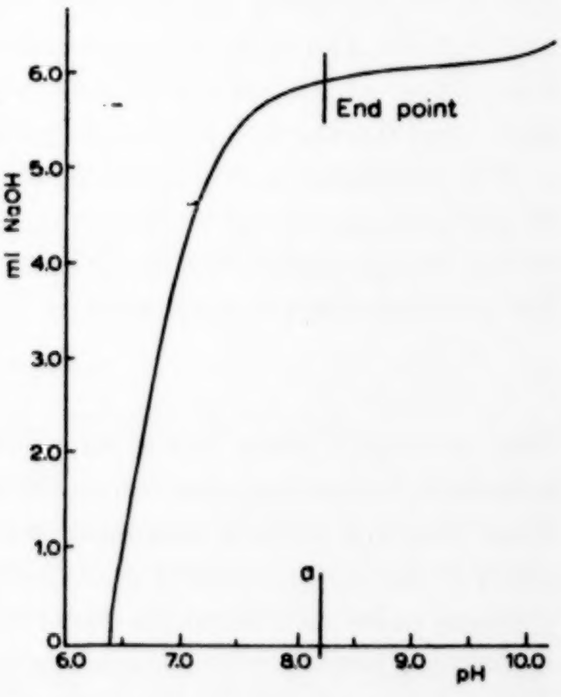

Fig. 2. Sample titration curve. a, pH of the citrate solution before addition of the sample.

titrations, the solution of the complexing agent can be adjusted to this pH before the addition of the sample and the titration.

The bias was determined using plutonium sulfate as the source of the hydrolyzable ion for both potassium oxalate and sodium citrate complexing solutions. The results are shown in Fig. 1. From this figure it is evident that sodium citrate is the better complexing agent: it has a smaller bias than potassium oxalate at all pH values investigated. Note also that for sodium citrate there is quite a wide pH range over which there is little bias.

All of the sodium citrate solutions prepared for the work described in this report had a pH ranging from 7.2 to 7.5. As far as bias considerations are concerned, the titration can be carried out within this pH range. However, if the pH is adjusted somewhere between 8.0 and 9.0, the end-point will occur on a steeper portion of the titration curve which makes the determination of the end-point easier. This is shown in a sample titration curve given in Fig. 2.

The data in Fig. 1 indicates that in the pH region where the bias is smallest there is still a bias of about 0.1 N. If the work being done requires results that are accurate to 0.1 N or less, a correction could be determined by running a series of known samples at a desired pH to obtain a mean bias value. This value could then be used to correct subsequent sample results.

Earlier it was mentioned that the plutonium sulfate used in this work was not acid free. This was compensated for by adjusting the pH of the complexing solution being studied to a higher pH value than desired, then adding the sulfate. After it had dissolved, the pH of the solution was again determined. This was recorded as the pH at which the titration was carried out and at which the end-point was determined. A portion of a titration curve illustrating this method of correcting for acid in plutonium sulfate is shown in Fig. 3.

Along with the investigation of complexing agents to eliminate interference from hydrolysis of plutonium, some exploratory work was done on a procedure involving precipitation of the plutonium with iodate, then titration of the free acid remaining in the filtrate. This procedure was developed by SMITH at Los Alamos[4]. Results obtained here using this procedure on spiked samples were low. Apparently the precipitate contained some acid iodate[9]. Therefore, work on the adaption of the procedure was not continued.

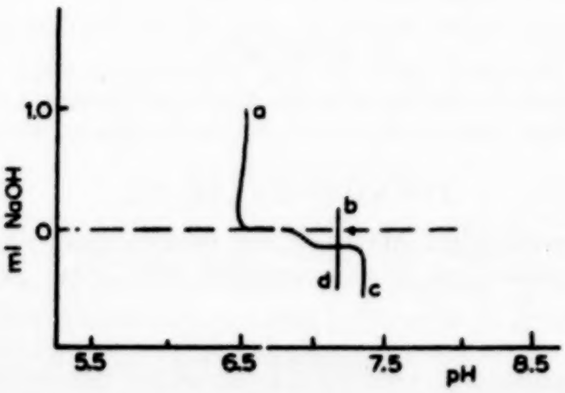

Fig. 3. Method used in correcting for residual sulfuric acid in plutonium sulfate. a, pH of citrate solution containing nitric acid and plutonium sulfate; b, pH of citrate solution containing plutonium sulfate; c, pH of citrate solution; d, pH used for determining end-point.

RESULTS

The day to day reproducibility of the method for plutonium-containing samples using sodium citrate as the complexing agent and a potentiometric end-point procedure was investigated. Three aliquots of a plutonium nitrate solution were run each day for six days. The average normality of the nitric acid in this sample was 7.46. The eighteen results ranged from 7.36 *N* to 7.55 *N*. The standard deviation was ±0.06 *N*.

TABLE I

EFFECT OF VARIATION IN PLUTONIUM AND ACID CONCENTRATIONS ON PRECISION OF RESULTS

Acid concentration N	*Mg Pu concentration*	*S.D. of % diff.*
6.92	22, 14, and 7	±0.73
3.90	22, 14, and 7	±1.69
0.79	22, 14, and 7	±6.02
6.92, 3.90 and 0.79	22	±4.35
6.92, 3.90 and 0.79	14	±3.71
6.92, 3.90 and 0.79	7	±2.23

An inspection of the data in Table I shows that the standard deviation increases, indicating a decrease in precision, when the acid concentration decreases and when the plutonium concentration increases. This behavior is what would be expected.

A series of experiments was undertaken to determine the effects of the concentration of plutonium and of acid on the precision of the results. Three levels of acid concentration were selected and at each acid level, samples containing three levels of plutonium concentration were run. Duplicate samples were run at each acid-plutonium concentration.

The standard deviations of the percent differences between the known and calculated normalities have been calculated. They are given in Table I, arranged to show the effect on the precision of the variation in the acid concentration when the plutonium concentration remains constant and *vice versa*.

SUMMARY

A method for the determination of free acid in the presence of plutonium has been evaluated. It involves the use of a complexing agent to prevent interference from the hydrolysis of plutonium. Of the complexing agents investigated, the citrate ion has been found the most efficient. The end-point is detected potentiometrically. The standard deviation, calculated from data obtained by the repeated analysis of a 7.46 *N* solution, is ± 0.06 *N*.

RÉSUMÉ

Une méthode potentiométrique de dosage d'acide libre, en présence de plutonium, a été mise au point. On propose l'ion citrate pour complexer le plutonium et empêcher ainsi son hydrolyse.

ZUSAMMENFASSUNG

Beschreibung einer potentiometrischen Methode zur Bestimmung von freier Säure in Gegenwart von Plutonium durch Komplexierung des Plutoniums mit Citrat (Verhinderung der Hydrolyse des Plutoniums).

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SOLVENT EXTRACTION BEHAVIOR OF SOME METAL-1-(2-PYRIDYLAZO)-2-NAPHTHOL CHELATES

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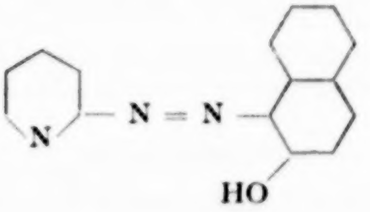
INTRODUCTION

PAN(1-(2-pyridylazo)-2-naphthol) is known to yield coloured chelates with cobalt[1], copper[2], palladium[3], uranium[4,5], and vanadium[6]. The compound has the structure:



In this paper, the quantitative reactions of PAN with various metallic ions are described with a view to extending the use of this reagent in inorganic colorimetric analysis.

EXPERIMENTAL

A 0.1% reagent solution was prepared by dissolving 100 mg of PAN (Tokyo Kasei Chem. Co.) in absolute methanol, filtering through glass wool, and diluting to 100 ml with methanol. All other chemicals used in this work were pure analytical reagents. All measurements were made with a Model EPV-2 Hitachi spectrophotometer, using 1-cm cells. A Beckman H-2 type pH meter was used. An aliquot of the slightly acid or neutral solution containing a microgram amount of metal was mixed with 5 ml of the buffer solution, and diluted to approximately 20 ml; 2 ml of 0.1% dye solution was added and the mixture allowed to stand for several minutes. Exactly 10.0 ml of the organic solvent was added to the mixture which was then shaken vigorously for 1–2 min. The solvent extract was centrifuged and the absorbance measured at a definite wavelength.

RESULTS AND DISCUSSION

The PAN extraction of about twenty metals has been studied. The reagent forms chelates with scandium, vanadium, manganese, iron, cobalt, nickel, copper, palladium, zinc, gallium, yttrium, silver, cadmium, indium, tin, platinum, gold, mercury, lead, bismuth, lanthanum, cerium, thorium and uranium. The colour reaction is particularly sensitive for manganese, cadmium, zinc, indium, gallium, mercury and iron in addition to cobalt, vanadium, copper, palladium and uranium. Table I records the colour reactions and solubility in various common organic solvents.

The absorption spectra of the metal chelates are shown in Fig. 1. The reagent solution itself shows a pale yellow coloration in acid or neutral solution. All the ions

TABLE I

SOLUBILITY

Metal	*Carbon tetrachloride*	*Benzene*	*Chloroform*	*Ether*	*Isoamyl alcohol*
Ga	—	—	Red	—	Red
In	—	—	Red	—	Red
Cu	—	Red	Red	—	Red
Bi	Yellow	Yellow	Yellow	Yellow	Orange red
Ni	Red	Red	Red	—	—
Zn	Red	Red	Red	—	Red
Fe(III)	Dull red	Dull red	Dull red	Red brown	—
Hg(II)	Red	Red	Red	—	Yellow
Mn	Red	Wine red	Red	Red	Orange
Co	—	Green	Brown	—	Green
Cd	Red	Red	Red	Red	—
Pb	—	—	Orange red	Orange	—
Ce(III)	Orange yellow	Orange	Orange	Orange yellow	Orange yellow
Y	Yellow	Yellow	Yellow	Yellow	Yellow
La	—	—	—	Orange yellow	—

Ga ~ Hg, pH 5.5; Mn ~ La, pH 9.0

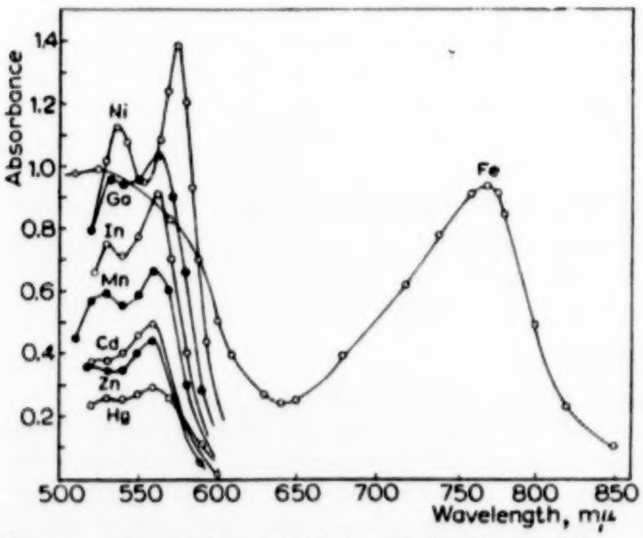


Fig. 1. Absorption spectra: Ni–benzene, Mn–ether, Ga, In, Cd, Zn, Hg, Fe–chloroform against reagent.

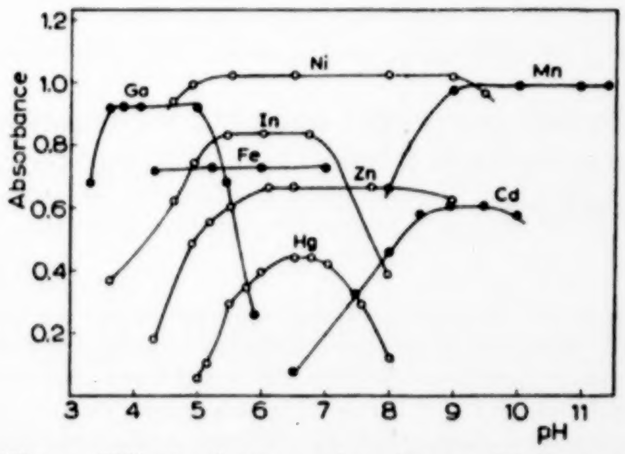


Fig. 2. Effect of pH on absorbance. Ni, 12 μg benzene extract; Mn, 9.5 μg ether extract; Ga, 30 μg In, 48 μg Fe, 25 μg Zn, 8.4 μg Cd, 14 μg Hg, 20 μg chloroform extract respectively.

showed in Fig. 1 formed red precipitates with the dye, except iron, which formed a dull red precipitate.

TABLE II

MOLAR EXTINCTION COEFFICIENT

Metals	*Molar extinction coefficient*	*Wavelength* $m\mu$
Mn	58500	560
Ni	50900	575
Cd	49000	560
Hg(II)	35300	560
Zn	28700	560
Ga	21500	560
In	19600	560
Fe(III)	16000	775

The pH of the solution has a considerable effect on the formation of chelates. Fig. 2 shows the variation in absorbance with varying pH of the metal chelates against a reagent blank. The data in Fig. 2 show that, with proper pH control, PAN is a very selective extraction agent. Beer's law was found to be obeyed by all metals listed in Table II. The molar extinction coefficients of the chelates calculated from Beer's law are listed in Table II.

Further work in this connection is in progress.

SUMMARY

The compound 1-(2-pyridylazo)-2-naphthol (PAN) has been found to be a sensitive and selective colorimetric reagent for manganese(II), indium, gallium, cadmium, zinc, nickel, mercury, and iron(III) if the pH is suitably controlled.

RÉSUMÉ

Le (pyridylazo-2)-1-naphthol-2 constitue un réactif colorimétrique sensible et spécifique pour le manganèse, l'indium, le gallium, le cadmium, le zinc, le nickel, le mercure et le fer(III).

ZUSAMMENFASSUNG

1-(2-Pyridylazo)-2-naphtol (PAN) hat sich als empfindliches und selektives Reagenz für die colorimetrische Bestimmung von Mangan(II), Indium, Gallium, Cadmium, Zink, Nickel, Quecksilber und Eisen(III) erwiesen.

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PHOTOMETRIC TITRATION OF CALCIUM IN BLOOD SERUM WITH ACID ALIZARIN BLACK SN AS METALLOCHROMIC INDICATOR

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The classical methods for determining calcium in blood serum are largely based on precipitation of the calcium as oxalate and subsequent titration with standard permanganate. Several methods based on complexometric titration of the calcium have been described more recently. Thus ELLIOTT[1] made use of the conventional murexide indicator in his procedure. However, this indicator is unstable and it is the experience of many that the end-point is difficult to judge; moreover in the presence of magnesium it has been shown that the colour change is gradual and indistinct[2] and also somewhat inaccurate[3]. REILLEY *et al.*[4] and some others[5] proposed that Calcon should be used as indicator in the direct titration of calcium in serum. REILLEY's method requires 1 ml of serum for each determination and shows a deviation ± 2.5% between duplicate determinations. HUNTER[6] has described an indirect photometric titration procedure for calcium and magnesium in blood serum which employs the conventional Eriochrome Black T and Murexide indicators. 0.2–0.3 ml samples are used and the calcium procedure is said to have an inherent error of ± 2%.

The indicator Calcein has been much favoured by many workers using visual and fluorimetric end-points[7–11]; the action of this indicator for pure calcium solutions has been commented on adversely elsewhere[3]. Other workers have preferred to use Patton and Reeder's indicator[12].

In the previous paper[13] we have investigated the reactions which occur between calcium and the closely related tris-hydroxy bis-azo dyestuffs Acid Alizarin Black-SN and -SE. In this communication we have sought to apply the former indicator to the determination of calcium in blood serum. In order to eliminate personal errors as much as possible we have applied a spectrophotometric procedure, for detection of the end-point.

By the procedure outlined below we have found it possible to determine calcium in only 0.1 ml or less of serum with an accuracy that is well within the limits required for clinical purposes. The procedure is rapid and can be employed where only 50 μl of solution are available.

In preliminary experiments we employed diethylamine to buffer the diluted serum solution since this buffer proved satisfactory in pure calcium solution. It was found here, however, that considerable reversion of colour occurred near the end-point.

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Finally, sodium hydroxide was selected as most suitable for pH adjustment, because it did not cause premature end-points; the colour contrast and consequent increase in optical density were not so pronounced as with diethylamine.

A method of standard addition was used to evaluate the results, for the classical method based on oxalate and permanganate was found to be too tedious and inaccurate for our purpose. A sample of serum was first titrated alone and subsequently an identical sample of the serum to which a known amount of standard calcium solution had been added was titrated in the same way. The recovery of added calcium agreed well with its known equivalence and hence it was inferred that the recovery of serum-calcium was also within limits of accuracy. Similar results were obtained when the standard addition was made to the freshly titrated serum solution, *cf.* Table I. Deproteinisation as advocated by HUNTER[6] was not found to be necessary for any of the sera examined. From these results it will be observed that the mean recovery of added calcium is 0.1 ml of $2.5 \cdot 10^{-3}$ *M* solution, *i.e.* 100%. The reproducibility of results may vary from 0.00 mequiv./l to 0.19 mequiv./l between duplicate determinations in the most unfavourable case. The mean difference, which reports a truer assessment of the precision of the method, is 0.07 mequiv./l, *i.e.* 1.5%.

TABLE I

THE DETERMINATION OF CALCIUM IN VARIOUS SERA WITH AND WITHOUT ADDITION OF 0.1 ml OF $2.5 \cdot 10^{-3}$ *M* $CaCl_2$

Serum	*Serum Ca^{+2} found mequivs./l*	*Added Ca^{+2} found ml*	*Serum*	*Serum Ca^{+2} found mequivs./l*	*Added Ca^{+2} found ml*
1	5.49	0.108	7	4.27	0.101
	5.49	0.098		4.46	0.097
2	5.31	0.093	8	4.60	0.096
	5.21	0.098		4.65	0.096
3	4.60	0.100	9	4.37	0.106
	4.65	0.101		4.27	0.108
4	4.70	0.099	10	4.84	0.103
	4.79	0.094		4.79	0.104
5	4.74	0.099	11	4.70	0.097
	4.74	0.101		4.65	0.102
6	3.48	0.101	12	5.07	0.101
	3.62	0.099		5.11	0.100

In order to determine the blank on reagents, etc. which, if not accounted for, would yield a high recovery of calcium in the serum determination or yield low equivalence for the EDTA solution if this were standardised directly against calcium in pure solution, the following procedure was adopted. An aliquot of standard calcium was titrated in pure solution with addition of the standard amount of all the reagents used in the serum analysis and the equivalence point was noted. Then another identical aliquot of calcium was added and the end-point was again found. The process was repeated with a third aliquot. The second and third titres were always found to be substantially the same and less than the first titre; the blank on the reagents is accounted for by this difference. *cf.* Table II.

For the purposes of this determination, it is not necessary to calculate the molarity of the EDTA since the mean subsequent titre, *cf.* Table II gives the amount of EDTA equivalent to 0.1 ml of $2.5 \cdot 10^{-3}$ *M* calcium chloride, *i.e.* 0.1 ml of solution containing 5 mequiv./l.

TABLE II

STANDARDISATION AND BLANK DETERMINATION

$2.5 \cdot 10^{-3}$ M Ca^{+2} taken (ml)	*EDTA used ml*	
0.100	0.108	First titre, includes blank
0.100	0.110	Second titre
0.100	0.106	Third titre
0.100	0.102	Fourth titre
0.100	0.110	First titre includes blank
0.100	0.108	Second titre
0.100	0.110	First titre includes blank
0.100	0.107	Second titre
0.100	0.105	Third titre

Mean first titre = 0.109 ml
Mean subsequent titre = 0.106 ml
Mean "blank" = 0.003 ml

0.106 ml EDTA = 5.0 mequivs./l calcium in a 0.10-ml sample

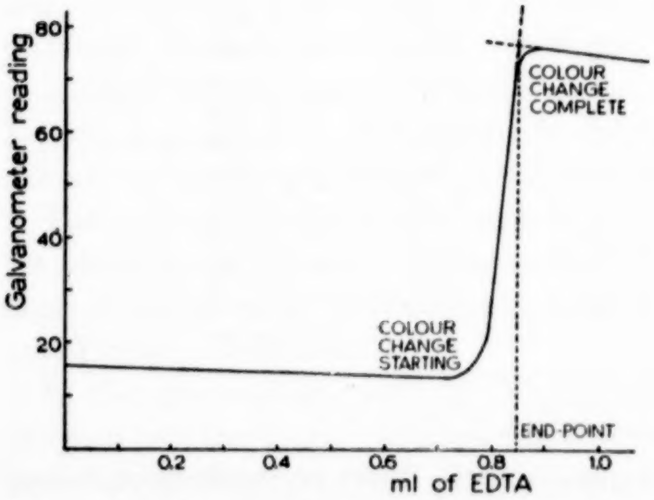

Fig. 1. Complexometric titration of Ca^{+2} with AABSN as indicator in *M*/400 solution.

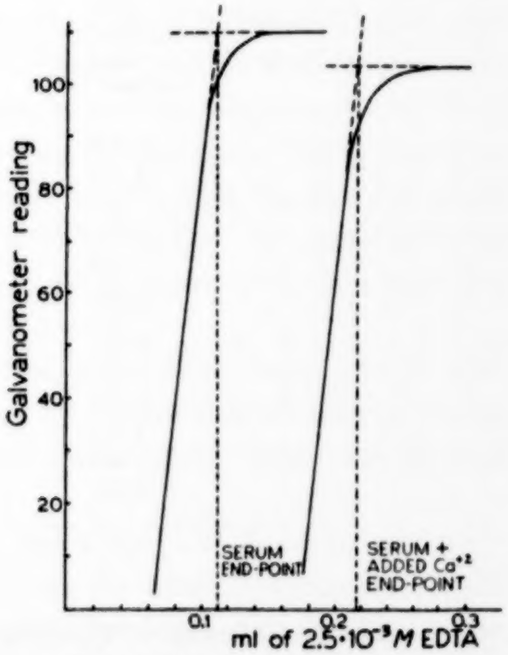

Fig. 2. Determination of Ca^{+2} in serum and with added 0.1 *N* mequiv. Ca^{+2}.

In these experiments an inexpensive commercial photo-electric titrator was used to detect the end-point. Fig. 1 shows the complete titration curve for a pure calcium solution; Fig. 2 shows the titration curve for calcium in 0.1 ml of a typical serum alone and in an identical aliquot with added 0.1 ml of $2.5 \cdot 10^{-3}$ *M* calcium chloride. Optical measurements were made with the No. 608 filter (660 mμ), thus following the appearance of the blue form of the metal free-indicator[9]. The titrations were made by means of a standard micro-syringe pipette (capacity 500 μl) and 4-ml titration vessel.

Although it was not always essential, a small amount of triethanolamine was added in all serum analyses to prevent interference by small amounts of metals such as iron etc. which still interfere even at the pH of the calcium determination. When the apparatus has been set up and the preliminary standardisation of the EDTA has been done a determination can readily be carried out within 10 min.

EXPERIMENTAL

Apparatus

Photoelectric titrator, (Evans Electro-selenium Ltd. Harlow, Essex) with Nr. 608 (660 mμ) filter and 4-ml titration vessel, 0.1-ml capacity wash-out pipettes and 2 Agla (Burroughs-Wellcome) glass syringes, capacity 500 μl.

Reagents

$2.5 \cdot 10^{-3}$ M Calcium chloride: 250.2 mg of oven dried (120°) AR grade calcium carbonate were transferred with water to a 600-ml beaker. Deci-normal hydrochloric acid, 60 ml was added carefully and the beakers were covered with a clock-glass till effervescence was finished. The contents of the beaker were then boiled gently to expel carbon dioxide. The surface of the clock glass was washed and the solution and washings were diluted to volume in a 1-l volumetric flask.

$2.5 \cdot 10^{-3}$ M EDTA (approx.): 93 mg of the dihydrated disodium salt of EDTA were dissolved in glass-distilled or deionised water and made up to 1 l. This solution was standardised as described subsequently.

N Sodium hydroxide: 40 g of NaOH dissolved and made up to 1 l with water.

$2 \cdot 10^{-1}$ M Triethanolamine: 3% aqueous solution.

Acid Alizarin Black SN: 0.1% aqueous solution. The indicator is now available from Hopkin and Williams Ltd., Chadwell Heath, Essex. The solution is indefinitely stable with only very slight deterioration after several months.

Procedures

(*a*) *Determination of blank and standardisation of EDTA.* 100 μl of $2.5 \cdot 10^{-3}$ *M* calcium chloride solution were delivered into 2.5 ml of distilled water in the 4-ml titration vessel by means of the syringe burette. 1 drop (0.05 ml) of $2 \cdot 10^{-1}$ *M* triethanolamine and 0.5 ml of *N* sodium hydroxide were added and the rotor of the magnetic stirrer of the instrument was activated to stir the solution. Finally 3 drops of indicator solution were added.

With the 660-mμ filter in position, the instrument diaphragm was adjusted to give an optical density reading of *ca.* 15. The $2.5 \cdot 10^{-3}$ *M* EDTA was then added slowly from the second syringe burrette with the tip well immersed below the surface of the liquid. As will be seen from Fig. 1, titration first results in a progressive decrease in optical density due to dilution since the indicator complex is not affected in this region. When the steep part of the curve was reached, optical density measurements were recorded after the addition of each 50 μl of titrant. The optical density quickly reaches a maximum and then decreases slightly (dilution effect) with further addition of titrant. The point of juncture of the two extrapolated slopes corresponds to the end-point of the titration.

The blank was determined by addition of a further 100-μl aliquot of $2.5 \cdot 10^{-3}$ *M* calcium solution and continuation of the titration to the next end-point. The difference between the two titres corresponds to the blank on the buffer etc. If necessary several other aliquots may be added to obtain a more representative value for the "mean subsequent titre" which corresponds to the true equivalence of 100 μl of $2.5 \cdot 10^{-3}$ *M* calcium chloride.

(*b*) *Determination of calcium in serum.* 100 μl of serum were added to the titration vessel from a wash-out pipette by means of distilled water to a total volume of 2.5 ml.

The solution was stirred gently by means of the magnetic rotor and was then treated with 1 drop of $2 \cdot 10^{-1}$ M triethanolamine, 0.5 ml of N sodium hydroxide and 3 drops of Acid Alizarin Black SN indicator. The rest of the titration was effected as described above.

Calculation

$2.5 \cdot 10^{-3}$ M calcium solution contains exactly 5 mequiv./l of calcium. Thus with 100-μl aliquots of serum and calcium.

$$\text{Calcium in serum (mequiv./l)} = \frac{5 \times (\text{EDTA consumed by serum} - \text{blank})\mu\text{l}}{\text{Mean subsequent titre against standard calcium}}.$$

The performance of any particular type of serum may be checked by adding 100 μl of $2.5 \cdot 10^{-3}$ M calcium to the freshly titrated serum sample. The value obtained should correspond to the mean subsequent titre obtained in the blank/standardisation procedure. If any slight discrepancy of analytical significance occurs, standardisation of the EDTA should be made against this latter value.

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SUMMARY

A method is described for the complexometric determination of calcium in blood serum. The procedure requires only 0.1 ml or less of serum and shows a mean precision between duplicate determination of $7 \cdot 10^{-2}$ mequiv./l, *i.e.* 1.5%. The sensitive new indicator Acid Alizarin Black SN is used in conjunction with a simple photoelectric titrator for the purpose of this determination.

RÉSUMÉ

Une méthode est décrite pour le dosage complexométrique du calcium dans le sérum sanguin. Le noir acide d'alizarine SN est utilisé comme indicateur; le point final est déterminé photométriquement.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur komplexometrischen Bestimmung von Calcium in Blutserum mit Alizarinschwarz SN (Säure) als Indikator. Der Endpunkt wird photometrisch bestimmt.

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DETERMINATION OF LEAD AND TIN IN LEAD–TIN SOLDER ALLOYS BY CONTROLLED-POTENTIAL ELECTROLYSIS

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The determination of lead in lead–base alloys is based on its precipitation as sulphate, after the dissolution of the alloy with a mixture of hydrobromic acid and bromine and after the successive volatilization of tin and antimony as bromides[1].

This method is time-consuming but gives highly accurate results and should be preferred to other gravimetric methods. To cut down the time required, recourse is often had to the titration of lead by molybdate[2] (even if this calls for an external indicator) or to direct[3] or back[4] titration with ethylenediaminetetraacetic acid and in the presence of Eriochrome Black or murexide as indicator. A further method used is the precipitation of lead by sulfuric acid after dissolution of the alloy with nitric and hydrofluoric acids[5].

To dissolve lead–base alloys, concentrated boiling sulfuric acid, to which potassium bisulfate or pyrosulfate is added to facilitate the attack is often used; lead is converted to a mixture of bisulfate and sulfate while the other elements are converted to their respective sulfates.

This type of dissolution seemed more advantageous and it has been suggested that the lead sulfate be dissolved with ammonium tartrate and the lead deposited by controlled potential electrolysis[6].

We have already shown[7] that lead can be deposited from a tartaric acid solution (adjusted to pH 5 with ammonia) at a cathode potential of —0.65 V *vs.* S.C.E. without any of the washing losses complained of by other authors[6,8].

However, at pH 5 not all the lead sulfate coming from the dissolution of the alloy is usually dissolved; for complete dissolution a pH of 7–8.5 is required, depending on the amount of lead and other elements present in the alloy.

At these pH values, lead deposits in a more adherent and compact form than at pH 5. However, deposition is not complete, especially if the solution pH is greater than 7.8, and it is not advisable to deposit Pb at a cathode potential more negative than —0.65 V *vs.* S.C.E. because antimony might co-deposit. On the other hand, with a pH of *ca.* 5 and —0.65 V *vs.* S.C.E., lead deposits completely and none is lost in the washing. It is therefore necessary to start the electrolysis of lead at a pH value of 7.2–8.5 and end the process at a pH of 4.8 – 5.3. The pH value is corrected during electrolysis by additions of diluted HCl (1:1) and is facilitated by the presence of succinic acid ($pK_1 = 4.5$, $pK_2 = 5.6$) which has a remarkable buffer capacity. If required, after an initial approximate correction with the diluted HCl a further adjustment of the pH may be done with NH_3 and HCl (1 + 1).

To prevent the anodic deposition of lead as dioxide, hydrazine hydrochloride is added to the solution as an anodic depolarizer; in any case, should some lead deposit on the anode at the beginning of electrolysis it re-dissolves when the electrolysis is about to end and deposits as metal on the cathode.

The electrodes used are 50 mm high and their diameter is 35 mm for the anode and 53 mm for the cathode. Stirring of the liquid is magnetic. Current intensities mentioned later in this paper refer to these electrodes and with different sizes of electrodes, other current intensities may possibly result. If deposited at pH 7.2–8.5 lead may damage the platinum cathode which should therefore be copper-plated before electrolysis.

With lead–tin solder alloys containing 2% of antimony, we have also examined the simultaneous electrolytic determination of tin. To this end, antimony is oxidized immediately after sample dissolution, otherwise it would partially co-deposit with tin. To deposit tin, the solution from which lead was deposited is simply acidified with hydrochloric acid and electrolyzed at a cathode potential of —0.65 V *vs.* S.C.E. A smooth platinum gauze is required; if it is sanded, tin should preferably be deposited on a copper-plated gauze.

The small amounts of copper, and possibly of silver and bismuth, present in the alloy deposit together with lead and must be removed if the correct percentage of lead is to be obtained. In a previous paper[9] a method was described for the electrolytic determination of the sum of said elements.

METHOD OF ANALYSIS

Reagents

Wash solution for cathode deposits: distilled water containing 1 drop conc. NH_3 per l.

Dissolving the sample and preparing the solution

Weigh 1 g of alloy, place in a 400-ml tall-form beaker, add 2 g of potassium pyrosulfate and 15 ml of concentrated H_2SO_4, $d = 1.83$. Heat on a Bunsen burner, at first moderately and then strongly until the sulfuric acid fumes rise to the upper section of beaker and partly recondense on the walls: at this point, sample dissolution is complete even though the alloy may appear to be dark. The volume of liquid in the beaker must be 6–8 ml; do not overconcentrate otherwise during the subsequent operations tin will not dissolve. Allow to cool without covering the beaker with a watch-glass. Slowly and cautiously add 25 ml of diluted HCl (1 : 3), by running down the beaker walls and stir.

Next, drop by drop and stirring, add 10–12 drops of 5% potassium permanganate solution. Dissolve 8 g of tartaric acid in about 25 ml of distilled water and pour this solution down the walls of the beaker. Then, wash the walls with distilled water. Add concentrated NH_3 ($d = 0.88$) in an amount slightly greater than actually needed to dissolve all the lead sulfate; the solution obtained must be perfectly clear and is bluish if copper is present. The pH of this solution varies from 6 to 8.5, depending on the amount of lead present. Ammonia is added using a Ranvier dropping bottle.

To the solution, add 2 g of succinic acid then, little by little, 1 g of hydrazine dihydrochloride. Hydrazine causes the reduction of copper, if any, and the consequent decoloration of the solution. If the pH decreases so much that lead sulfate re-precipitates, add some concentrated NH_3 until all the precipitate has dissolved, being careful to keep any excess NH_3 to a minimum.

Adjust the pH using narrow-range pH test papers which have been checked by a pH-meter. Corrections are made with diluted HCl (1 : 1) and with concentrated or dilute NH_3 (1 : 1).

The solution should possibly have a pH value of 7.2–7.3 or, should a higher pH be required to keep the lead sulfate in solution, the pH may be increased but only up to the value at which no precipitation occurs (up to 8.5). Even if the solution is rather cloudy on account of lead sulfate, the subsequent electrolysis may be carried out without any trouble because while it takes place the salt dissolves. Should cloudiness be due to hydroxides of tin and antimony which have precipitated following some previous mishandlings, a new sample dissolution must be made. When the amount of lead present is small, a complete dissolution of sulfate is possible at pH 5–6, but the pH is then again adjusted to 7.2–7.3.

Lead is then deposited as metal on the previously copper-plated cathode.

Electro-deposition of lead

The electrolysis of Pb is carried out at a cathode potential of —0.65 V *vs.* S.C.E. but, initially, this potential is kept at a less negative value so as to have a current intensity of 0.3–0.4 A; the cathode potential is then gradually increased to —0.65 V *vs.* S.C.E.

As the electrolysis proceeds current density decreases, and at the end it might be as low as less than 0.01 A. In other cases, namely, when the initial pH of the solution electrolyzed is higher than 7.8, it drops to about 0.06–0.08 A.

At this point, without stopping the electrolysis, adjust the pH of the solution to about 5 by adding dilute HCl (1 : 1). Test the solution with narrow-range test papers which have been previously checked at pH 5 using a pH-meter.

During the correction of pH, current intensity remains at around 0.01 A if this minimum value had already been reached; otherwise it increases, in which case it must be kept below 0.1–0.15 A by making the cathode potential less negative. The cathode potential is then progres ively increased to —0.65 V *vs.* S.C.E., and kept at this level, until the current intensity does not drop to a minimum value (generally less than 0.01 A) where it remains constant.

Electrolysis ends 15 to 20 min after the minimum current intensity value is reached. Wash in the usual manner[6,7], dry and weigh. Electrolysis lasts for about 60 min; the deposit is highly compact and adherent.

When the electrolyzed solution has a pH greater than 7.3 and the current intensity does not drop to 0.01 A, correction of the pH during electrolysis may be made more profitably in two stages: the adjustment from the initial pH to a pH of 7.3–7.4, 15–20 min after the start of electrolysis (making the cathode potential less negative if current intensity increases beyond 0.3 A) then dropping back to a pH of approximately 5 when intensity falls to about 0.01 A. By proceeding as described, less time is required for the electrolysis.

Electro-deposition of tin

To the solution remaining after deposition of lead, add 30 ml of concentrated HCl, 0.2 g of hydrazine dihydrochloride. Start the electrolysis at such a cathode potential that current intensity does not exceed 1 A. Generally, electrolysis is initially accompanied by a strong development of gas that diminishes and almost disappears within

2–3 min. When the current intensity tends to drop below 1 A the cathode potential is made more negative until the value of —0.65 V *vs.* S.C.E. is reached.

When, after dropping, current intensity levels off at a constant value, (generally, 0.06 to 0.03 A) wait 15 more minutes, then wash, dry and weigh in the usual manner. This electrolysis takes about 60 min, *viz.*, approximately the same time as the lead deposition. If the time required to weigh and dissolve the sample is added, plus the time needed to prepare the solution for electrolysis, the result is that the two determinations (Pb and Sn) can cumulatively be carried out in about three hours.

The cathode is cleaned with dilute HNO_3 (1 : 1) containing tartaric acid, then washed with distilled water and cleaned once more with dilute lukewarm HCl (1 : 1).

Results

Table I gives the results found by analysing synthetic solutions obtained by dissolving, according to the method described, weighed quantities of the pure metals. Agreement between the weighed quantities and those found is excellent.

From tests Nos. 7, 8 and 14 it can be seen that even 0.8 g of lead or tin can be practically completely deposited.

TABLE I

ANALYSIS OF SYNTHETIC SOLUTIONS

(All weights in g)

	Pb		*Sn*		*Sb*
	Weighed	*Found*	*Weighed*	*Found*	*Weighed*
1	0.1201	0.1211	0.4205	0.4207	0.0027
2	0.2013	0.2011	0.2898	0.2902	0.0052
3	0.3826	0.3824	0.1298	0.1292	0.0120
4	0.2524	0.2520	0.3238	0.3242	0.0118
5	0.3020	0.3020	0.2225	0.2219	0.0076
6	0.1738	0.1735	0.3204	0.3198	0.0068
7	0.8007	0.8004	0.2015	0.2019	0.0101
8	0.7771	0.7765	0.1992	0.1992	0.0199
9	0.7025	0.7023	0.3248	0.3248	0.0106
10	0.6030	0.6027	0.4064	0.4062	0.0196
11	0.6002	0.5999	0.3868	0.3870	0.0210
12	0.4066	0.4065	0.5653	0.5659	0.0216
13	0.4039	0.4035	0.5990	0.5995	0.0215
14	0.2014	0.2012	0.7921	0.7924	0.0208

TABLE II

ANALYSIS OF SOLDER N. 127a (N.B.S.)

Composition	*No.*	*Weighed g*	*Results*	
			Pb+Cu+Bi+Ag	*Sn*
Pb = 69.005 (by difference)	1	1	69.01	30.08
Cu = 0.004 Sb = 0.79	2	1	69.10	30.04
Bi = 0.036 Ni = 0.002	3	1	69.06	30.05
Ag = 0.004 As = 0.129	4	1	69.04	30.03
69.049 Sn = 30.03	5	1	69.08	30.02

The percentage of solder 127 A (N.B.S.) has been computed by difference; also in this case agreement of results is excellent, as shown in Table II.

Determination of lead in lead-base alloys

The method described for the determination of lead is also applicable to almost all other lead-base alloys, provided that the weighed amount is not greater than 0.5 g. In fact, if the antimony present in the solution exceeds 0.1 g and lead is more than 0.60 g the results obtained begin to be too high because antimony tends to co-deposit from the ammoniacal solution.

The chemical dissolution of 0.5 g of alloy is carried out with 10 instead of 15 ml of concentrated sulfuric acid.

As mentioned earlier, small quantities of copper, bismuth and silver (if present in the alloy) co-deposit with lead; the sum of these elements may be determined by a previously described method[9] and subtracted from the percentage of lead.

Listed in Table III are the results obtained with synthetic samples, and in Table IV those with White Metal A sample No. 177 (British Chemical Standards). The Certificate of Analysis for this sample tabulates the lead values from ten analyses performed by different laboratories: the lowest percentage is 82.20%, the highest 82.93%, and the overall average 82.60%.

TABLE III

ANALYSIS OF SYNTHETIC SAMPLES

(All weights in g)

No.	*Pb* *Weighed*	*Pb* *Found*	*Sn* *Weighed*	*Sb* *Weighed*
1	0.4906	0.4902	0.009	0.0168
2	0.4876	0.4876	0.0133	0.0206
3	0.4486	0.4480	0.0370	0.0312
4	0.4071	0.4074	0.0451	0.1012
5	0.3995	0.3999	0.0310	0.1002
6	0.3506	0.3503	0.1454	0.0702
7	0.3996	0.3995	—	0.1000
8	0.5022	0.5021	—	0.0248

TABLE IV

ANALYSIS OF WHITE METAL N. 177A (B.C.S.)

Composition	*No.*	*Weighed g*	*Pb+Cu+Bi %*
Pb = 86.60 (82.20+82.93)	1	0.5	83.20
Cu = 0.33	2	0.5	83.19
Bi = 0.03 Zn = 0.08	3	0.5	83.20
Sb = 12.04 Fe = 0.06	4	0.5	83.17
Sn = 4.64 As = 0.06	5	0.5	83.23

Maximum and minimum percentages for antimony and tin are: Sb = 11.91%–12.20%; Sn = 4.16%–4.94%. The determination of lead according to the method described above gave: Pb+Cu+Bi = 83.20% and, after subtracting Cu+Bi, we have Pb = 82.84%. Since the sum of all percentages quoted on the Analysis Certificate is 99.84, the percentage we found is probably the most acceptable one.

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SUMMARY

Lead is determined in lead-tin alloys, by dissolving the sample with sulfuric acid and potassium pyrosulfate and controlled potential electrolysis after addition of tartaric acid and dissolution of lead sulfate with ammonia.

Tin can be determined by electro-deposition from the same solution after acidification with hydrochloric acid, if antimony is oxidized with permanganate and is less than 200 mg.

RÉSUMÉ

Une méthode est proposée pour le dosage du plomb et de l'étain dans leurs alliages, par électrolyse à potentiel contrôlé. On dépose d'abord le plomb, en présence d'acide tartrique et d'ammoniaque, puis on électrolyse l'étain, après avoir acidifié par l'acide chlorhydrique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Blei und Zinn in Legierungen durch Elektrolyse bei kontrolliertem Potential. Zuerst wird Blei aus einer ammoniumtartrathaltigen Lösung abgeschieden und nach Ansäuern mit Salzsäure das Zinn.

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OXYDATION DE QUELQUES SYSTÈMES INORGANIQUES PAR LE TÉTRACÉTATE DE PLOMB

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Le tétracétate de plomb ($PbAc_4$) est, grâce à ses propriétés oxydantes, un réactif souvent utilisé en chimie organique. Il a été employé pour la première fois par Dimroth et F. Frister[1]. Ils ont constaté que ce composé réagit différemment et souvent de façon plus sélective que le peroxyde de plomb utilisé jusqu'à cette époque. D'autres

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travaux ont été publiés par Criegee[2–5], signalant notamment la réaction caractéristique du tétracétate de plomb sur les α-glycols. Malgré les nombreuses applications que le tétracétate de plomb a trouvé en chimie organique, peu d'attention a été portée à son utilisation en chimie analytique. Ceci est dû surtout au fait que, pour obtenir un milieu non aqueux pour la préparation du réactif (afin d'éviter l'hydrolyse), on a ajouté à l'acide acétique glacial de l'anhydride acétique; ce dernier réagit lentement avec $PbAc_4$, qui fut alors considéré comme instable.

Tomíček et Valcha[6], dans le cadre de leur étude sur les titrages d'oxydo–réduction en solution acétique, ont constaté, que les solutions de tétracétate de plomb dans l'acide acétique glacial, en absence d'anhydride acétique, sont très stables. Ces solutions ont été utilisées pour les titrages directs de l'hydroquinone, de la tétrachlorohydroquinone, du pyrocatéchol, de l'acide ascorbique, du benzylmercaptan et indirectement de l'acide amygdalique. Ces auteurs ont étudié également les variations des potentiels d'oxydo–réduction, en fonction de la concentration en acétate et en acide perchlorique. En présence d'acide perchlorique, les valeurs du potentiel sont supérieures à 1.2 V; en présence d'acétate, elles sont inférieures à 1.08 V par rapport à l'électrode au calomel saturée.

Dans des travaux plus récents nous avons signalé la possibilité d'oxydation par $PbAc_4$ en milieu aqueux[7], dans les cas où la réaction d'oxydo–réduction est plus rapide que la réaction d'hydrolyse du sel de plomb tétravalent. Nous avons comparé le pouvoir oxydant du tétracétate de plomb et celui du periodate de potassium sur quelques α-acide-alcools et sur la mannite, en milieu aqueux, dans les mêmes conditions[8].

Dans ce travail nous avons étudié la possibilité d'oxydation des systèmes inorganiques réducteurs courants par $PbAc_4$, dans des solutions aqueuses acidifiées de manière appropriée par des acides minéraux. Nous avons constaté que l'oxydation des systèmes étudiés, par $PbAc_4$, dans les conditions citées, s'effectue quantitativement et si rapidement, qu'on peut l'utiliser pour les titrages directs potentiométriques, à la température du laboratoire, dans des larges limites d'acidité.

Un procédé rapide et simple est proposé pour la préparation du réactif, exempt de plomb(II).

PARTIE EXPÉRIMENTALE

Réactifs

Solution de sulfate de fer(II) (p.a. Merck) 0.05 *N* titrée par le dichromate de potassium[9].

Solutions de chlorure d'étain(II) et d'antimoine(III) (p.a. Merck) 0.05 *N* titrées par le bromate de potassium[9].

Solution de chlorure de titane(III) 0.05 *N* (préparée par dilution de $TiCl_3$ 20% p.a. Lachema) titrée par le dichromate de potassium[9].

Solution de chlorure de chrome(II) 0.05 *N* (préparée par réduction de $CrCl_3$ p.a. Merck en solution chlorhydrique 2 *N* par l'amalgame de zinc). Son titre a été déterminé au moyen de sulfate de fer(III) (obtenu par oxydation du sulfate de fer(II) par le dichromate de potassium) en milieu sulfurique 1 *N*[10].

Solution d'arsénite de sodium (préparée par dissolution de l'anhydride arséniaux As_2O_3 (p.a. Merck) dans l'hydroxyde de sodium 1 *N*[9]). Solution de tétracétate de plomb 0.1 *N* (préparation décrite ci-dessous). Le titre a été déterminé par le sulfate d'hydrazine[7].

Préparation de la solution de tétracétate de plomb

Le tétracétate de plomb s'obtient par réaction du minium (Pb_3O_4) avec l'acide acétique glacial, à chaud. Les solutions étalon de tétracétate de plomb peuvent se préparer soit par pesée du minium, que l'on traite ensuite par l'acide acétique glacial, soit en isolant les cristaux de $PbAc_4$ et en les dissolvant après recristallisation dans l'acide acétique glacial. Ce deuxième mode de préparation permet d'obtenir des solutions exemptes de plomb(II).

Nous avons ajouté à 1 l d'acide acétique glacial (chauffé à ébullition pendant 10 min et ensuite refroidi à 80° env.) le minium par petites quantités, en agitant énergiquement, jusqu'à coloration persistante. Nous avons constaté qu'il est possible de dépasser la température de 65° recommandée dans la littérature[11], sans que commence la réduction du tétracétate en train de se former (l'anhydride acétique capable d'oxydation n'étant pas présent), et sans que commence l'hydrolyse du réactif. La solution obtenue est filtrée à chaud sur entonnoir de Buchner; on laisse refroidir dans un récipient fermé, pendant au moins trois heures. Les cristaux formés pendant ce temps sont séparés par décantation, la solution résiduelle est concentrée en vue d'une nouvelle cristallisation, en séparant par distillation environ 2/3 de tout le volume de l'acide acétique. Cet acide distillé pourra être utilisé pour une nouvelle préparation du réactif. On laisse reposer la solution concentrée dans un récipient fermé, de préférence pendant une nuit. Puis on sépare de nouveau les cristaux par décantation et on les ajoute à la première partie de $PbAc_4$, conservé pendant ce temps dans un flacon bouché à l'abri de l'air humide sous un peu d'acide acétique, préalablement chauffé à ébullition. Si la liqueur surnageante est trouble, on répète la décantation avec un peu d'acide acétique préalablement chauffé à ébullition. On fait ensuite recristalliser tout le tétracétate de plomb obtenu. (Au cours de la concentration on distille l'acide acétique afin de l'utiliser pour les travaux suivants). Les cristaux obtenus sont ensuite dissous à une température de 50° env. dans l'acide acétique glacial. Après refroidissement, d'environ 24 h, tout le tétracétate en excès cristallise et la solution saturée surnageante a, d'après nos expériences, une concentration d'environ 0.13 *N*. Mais au lieu de procéder par pesée de la substance solide, il est préférable de préparer les solutions par dilution de la solution saturée. On porte alors 750 ml environ de solution saturée à 1 l par l'acide acétique glacial, chauffé à ébullition pendant 10 min et ensuite refroidi. Les solutions obtenues sont incolores, limpides; conservées dans des récipients hermétiquement bouchés, leur stabilité est pratiquement illimitée.

Appareils

Les titrages potentiométriques ont été effectués au moyen d'un pH-mètre EK/21 (Kovodružba Praha) en utilisant un fil de platine comme électrode indicatrice et une électrode au calomel, comme électrode de référence. Pour agiter le liquide, un agitateur électromagnétique a été utilisé; dans le cas de titrage en atmosphère inerte, le liquide a été traité par un courant d'azote.

RÉSULTATS

Dans ce travail nous avons suivi l'oxydation de Fe^{+2}, Sn^{+2}, Sb^{+3}, As^{+3}, Ti^{+3} et Cr^{+2} par $PbAc_4$ 0.1 *N* en milieu aqueux. L'oxydation s'effectue quantitativement et si rapidement, qu'on peut, dans des solutions acidifiées de manière appropriée, utiliser le tétracétate de plomb pour des dosages volumétriques et potentiométriques. Dans les solutions acidifiées par l'acide sulfurique, le plomb (produit de la réduction de $PbAc_4$) précipite comme sulfate de plomb $PbSO_4$, sans gêner le titrage. Le potentiel de l'électrode indicatrice se stabilise très vite et les résultats sont parfaitement reproductibles.

Les résultats et les conditions de titrages sont donnés dans le Tableau I. La différence relative moyenne a été calculée sur dix mesures différentes.

TABLEAU I

TITRAGE DE Cr^{+2}, Ti^{+3}, Fe^{+2}, Sn^{+2}, Sb^{+3} ET As^{+3} PAR LE TÉTRACÉTATE DE PLOMB 0.1 *N*

Substance déterminée (La valeur entre parenthèses indique la quantité de l'élément (en mg) correspondant à 1 ml de $PbAc_4$ 0.1 N)	*Quantité déterminée (mg)*	*Milieu*	*Potentiel d'inflexion (mV)*	*Variation du potentiel au point équivalent (mV/0.01 ml de réactif)*	*Erreur relative moyenne (%)*
Cr^{+2} (5.201)*	12–43	HCl 0.08–3 *N*	315 (HCl 0.25 *N*)	1500 (HCl 0.25 *N*)	0.23
Ti^{+3} (4.79)*	9–31	H_2SO_4 0.5 –4 *N* HCl 0.05–4 *N*	530 (HCl 0.2 *N*)	600 (HCl 0.2 *N*)	0.17
Fe^{+2} (5.585)	11–46	HCl 1–4 *N*	780 (HCl 2 *N*)	200 (HCl 2 *N*)	0.20
Sn^{+2} (5.935)*	13–52	H_2SO_4 0.25–4 *N* HCl 0.25–2 *N*	440 (HCl 1 *N*)	700 (HCl 1 *N*)	0.19
Sb^{+3} (6.088)	15–45	H_2SO_4 0.25–4 *N* HCl 0.35–6 *N*	815 (H_2SO_4 2 *N*)	120 (H_2SO_4 2 *N*)	0.12
As^{+3} (3.7455)	8–32	H_2SO_4 0.05–8 *N* HCl 0.005–8 *N*	600 (HCl 0.03 *N*)	400 (HCl 0.03 *N*)	0.22

* Titré en atmosphère inerte.

Nous supposons qu'il serait possible d'utiliser le tétracétate de plomb pour le titrage direct d'autres systèmes et pour des dosages microchimiques. Nos recherches dans ce domaine se poursuivent.

RÉSUMÉ

Les réactions d'oxydation du tétracétate de plomb avec As^{+3}, Sb^{+3}, Sn^{+2}, Fe^{+2}, Ti^{+3} et Cr^{+2} s'effectuent quantitativement et si rapidement, qu'il est possible de les utiliser pour des dosages volumétriques et potentiométriques directs. Les solutions de tétracétate de plomb ont une stabilité pratiquement illimitée. On envisage la possibilité d'oxydation d'autres systèmes inorganiques. La préparation du tétracétate de plomb est décrite.

SUMMARY

Reactions of lead tetraacetate with As^{+3}, Sb^{+3}, Sn^{+2}, Fe^{+2}, Ti^{+3} and Cr^{+2} can be carried out in aqueous solutions, containing a suitable amount of mineral acid. The quantitative course of the reactions can be used for a direct potentiometric determination with lead tetraacetate as a stable volumetric reagent. The preparation of Pb^{+2}-free solutions of lead tetraacetate is described.

ZUSAMMENFASSUNG

Die Oxydationen von As^{+3}, Sb^{+3}, Sn^{+2}, Fe^{+2}, Ti^{+3} und Cr^{+2} mit Bleitetraacetat verlaufen quantitativ und so schnell, dass sie zu direkten volumetrischen und potentiometrischen Bestimmungen

verwendet werden können. Lösungen von Bleitetraacetat sind praktisch unbegrenzt haltbar. Die Herstellung von Bleitetraacetat wird beschrieben.

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SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM IN MAGNESIUM-BASE ALLOY

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INTRODUCTION

In recent communications the use of neothoron [2-(*o*-arsonophenyl-azo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid] as a reagent for the spectrophotometric determination of uranium[1], beryllium[2], cerium[3], and lanthanum[4] has been reported. With zirconium neothoron gives a blue colour which is stable in strong acidic solution. In contrast to existing methods the procedure is simple and unaffected by many heavy metals. The use of neothoron as a reagent for the spectrophotometric determination of zirconium is described in this paper, together with a method which is applicable to the determination of zirconium in magnesium–base alloys *e.g.* ZK and EK alloys.

EXPERIMENTAL

Reagents

A neothoron solution (0.1%) was prepared by dissolving 0.1 g of pure crystals (Tokyo Kasei Chem. Co.) in distilled water and diluting to 100 ml. A standard solution of zirconium was prepared by dissolving 0.889 g of pure zirconium sulphate in distilled water which contained an appropriate amount of hydrochloric acid and diluting to 250 ml. This solution containing 0.912 mg of zirconium per ml was standardized gravimetrically. Buffer: The pH was adjusted by adding a mixed solution of hydrochloric acid (0.2 *N*)–potassium chloride (0.2 *N*). All other chemicals used in this work were pure reagents.

Apparatus and technique

A Hitachi EPV-2 spectrophotometer with 1-cm cells was used for all measurements. All solutions were diluted to a final volume of 25 ml before transfer to the absorption cells. The pH was measured with a Beckman H-2 type pH meter.

RESULTS AND DISCUSSION

Absorption curves. The absorption curves of the zirconium–neothoron complex are shown in Fig. 1. At 578 mμ, the complex shows maximum absorption against the reagent blank. The reagent has only a small absorption at this wavelength which was therefore chosen for all further work.

Effect of pH. The pH of the solution has a considerable effect on the colour intensity. Solutions containing the same amounts of zirconium and neothoron (in excess) were prepared at different pH values and their absorptions were measured. The results (Fig. 2) show that between pH 1.6 to 2.0 the absorption remained constant.

Effect of varying amounts of reagent. The absorptions of a series of solutions of pH 1.7,

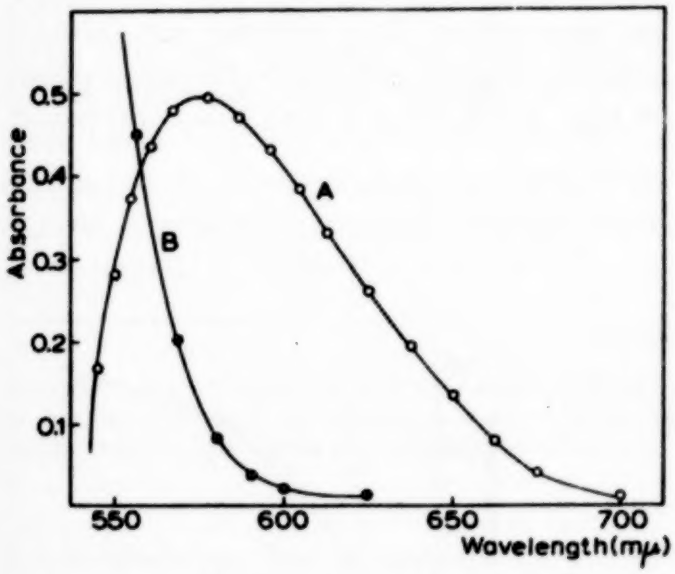

Fig. 1. Absorption spectra of zirconium–neothoron complex. A, zirconium–neothoron complex, 450 μg Zr/25 ml. B, neothoron.

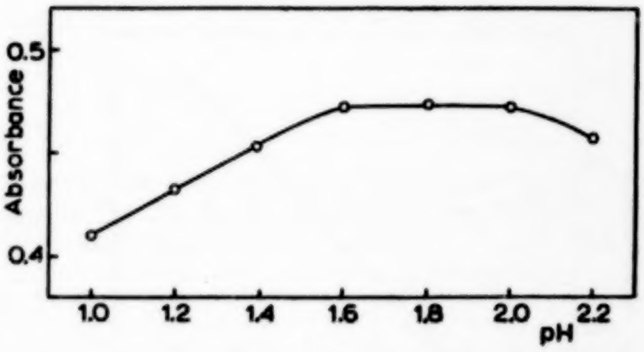

Fig. 2. Effect of pH on absorbance. $\lambda = 578$ mμ, 2 ml neothoron added.

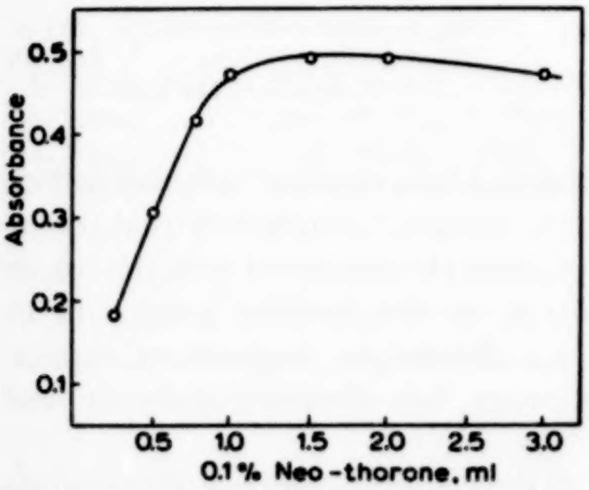

Fig. 3. Effect of neothoron concentration on absorbance. Zr, 450 μg. pH 1.72; $\lambda = 578$ mμ.

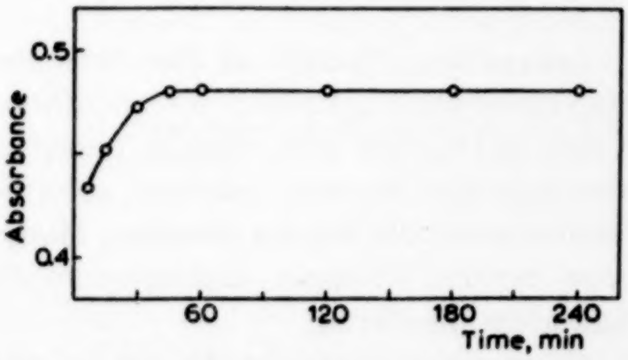

Fig. 4. Effect of reaction time. pH 1.72; $\lambda = 578$ mμ.

each containing 450 μg zirconium per 25 ml with varying amounts of reagent, were measured to determine a suitable concentration of the reagent. The results (Fig. 3) show that 2 ml of an aqueous 0.1% solution suffice to complex 450 μg of zirconium in 25 ml of solution. But a large excess of reagent caused a slight gradual decrease in the absorbance.

Effect of time of standing. The colour of the zirconium complex in aqueous medium was fully developed after 1 h, and the absorbance was unchanged for at least 4 h at room temperature (Fig. 4).

Beer's law. The validity of Beer's law for the system was investigated by the usual method at 578 mμ. The system obeys Beer's law in the concentration range 0–500 μg zirconium per 25 ml (Fig. 5).

Sensitivity. The molar extinction coefficient of the complex calculated from Beer's law is 2400, and the sensitivity of the colour reaction is 0.94 μg zirconium per cm^2 (according to Sandell's definition).

Procedure. An aliquot of several ml of test solution containing up to 500 μg zirconium was pipetted into a 25-ml volumetric flask. To the flask 5 ml of pH 1.7 buffer solution and 2 ml of 0.1% neothoron solution were added. The solution was diluted to 25 ml with distilled water. After 1 h, the solution was transferred to the absorption cell and the absorbance was measured at 578 mμ. A reference solution was prepared with reagent.

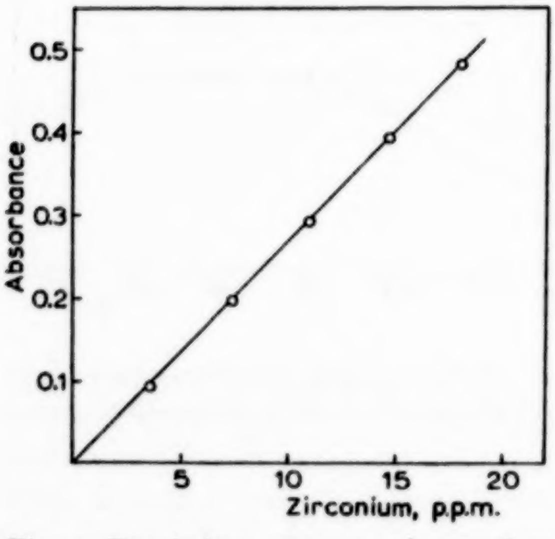

Fig. 5. Beer's law. pH 1.72; $\lambda = 578$ mμ.

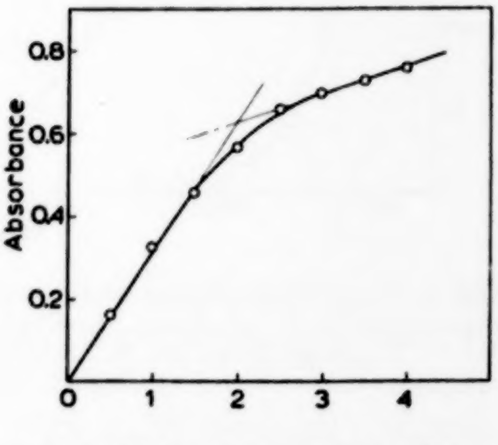

Fig. 6. Mole-ratio method. [Zr] = [neothoron] = $2.34 \cdot 10^{-3}$ *M*, pH 1.72; $\lambda = 578$ mμ.

Interferences. Nearly all the elements associated with zirconium were studied to determine their behaviour with neothoron under the optimum conditions used above. Citric and tartaric acid, oxalate, phosphate, and perchlorate interfered with the colour development. Acetate, sulphate, chloride, and nitrate as their sodium, potassium, or ammonium salts did not interfere. Many cations, *e.g.* aluminium, magnesium, copper, iron, cerium, titanium, and uranium did not interfere, but thorium, niobium, and tantalum interfered.

Composition of complex. The empirical formula of the coloured complex of zirconium was determined by the mole ratio method. Within experimental error the results (Fig. 6) suggest a 2 : 1 complex of zirconium with neothoron.

Determination of zirconium in ZK and EK alloys. To a 1.000-g sample in a 500-ml beaker, add 20 ml of 1 : 1 hydrochloric acid, warm on a hot plate until dissolved, cool, neutralize with ammonium hydroxide, and dilute to 200 ml in a volumetric flask. Transfer a 10.0-ml aliquot to a 25-ml volumetric flask, containing 5 ml of buffer solution (pH 1.6 to 2.0) and 2 ml of neothoron solution. Dilute to the mark and mix. After one hour, measure the absorbance of the sample against a blank of zirconium-free magnesium carried through all the steps of the procedure. The measurements were carried out in a 1-cm cell at 578 mμ. The concentrations of zirconium were estimated by interpolating the absorbance in the previously prepared calibration curves, and were compared with the results of a gravimetric estimation using phosphate method (Table I).

TABLE I

DETERMINATION OF ZIRCONIUM IN ZK AND EK ALLOYS

Samples	*Neothoron method* %	*Phosphate method* %
Zn, rare earth-free	0.78	0.75
ZK 1 (Zn, 5%)	0.18	0.18
ZK 2 (Zn, 6%)	0.93	0.91
EK 1 (r.e., 3%)	0.02	0.01
EK 2 (r.e., 3%)	0.70	0.67

SUMMARY

A rapid spectrophotometric determination of zirconium with neothoron is described. Large amounts of magnesium and moderate amounts of many heavy metals have no effect. The method is applicable to the direct determination of zirconium in magnesium-base alloys.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour un dosage rapide du zirconium, au moyen de néothorone. Elle peut être appliquée à des analyses d'alliages à base de magnésium.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur raschen Bestimmung von Zirkonium mit Neothoron als Reagenz. Die Methode lässt sich auch bei Magnesiumlegierungen anwenden.

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SEPARATION OF RADIOCOBALT FROM NICKEL

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INTRODUCTION

A reinvestigation of the classical cobaltinitrite method for the separation and estimation of cobalt in the presence of nickel is described in this study. This work was undertaken in conjunction with experiments in the nuclear physics field by CARVER AND TURCHINETZ[1] and PURSER AND TITTERTON[2], which imposed certain limiting conditions on the separation.

The nuclear problem involved the irradiation of nickel metal with both high energy γ radiation and fast neutrons. In the former case it was required to determine the ratios of the ^{58}Ni $(\gamma,p)^{57}$Co and ^{58}Ni $(\gamma,n)^{57}$Ni yields and in the latter, the ^{58}Ni $(n,np)^{57}$Co and ^{58}Ni $(n,2n)^{57}$Ni yields. Since the decay product from the 36 h ^{57}Ni is also 270 day ^{57}Co, it is apparent that separation of ^{57}Co immediately after irradiation enables measurement of both the (γ,p) and (n,np) yields respectively and another separation after one or two weeks measures the corresponding (γ,n) and $(n,2n)$ yields. The critical requirements for these determinations were, therefore, fairly rapid separation (< 1 h) and at the same time reasonably complete cobalt removal ($> 99\%$), immediately following the irradiations.

The quantity of nickel irradiated (~ 10 g) and the requirement for the separated cobalt to be in a suitable physical form for analysis by scintillation spectrometry indicated that the cobaltinitrite separation was the most suitable one. However, in analytical textbooks, it is usually stated that the precipitation step in this method takes an appreciable period of time. For example, SCOTT[3] states that the precipitating solution should be left for 6 h or preferably overnight, KOLTHOFF AND SANDELL[4] not less than 12 hours, HILLEBRAND, LUNDELL, BRIGHT AND HOFFMAN[5] 24 hours, and TREADWELL AND HALL[6] 24 hours. The methods described in these textbooks also differ in the respect that Scott recommends that the solution be brought to the boiling point immediately before the precipitation step and retained at this temperature for a 30-min period during precipitation. The other texts do not mention this requirement.

RESULTS AND DISCUSSION

A series of experiments was performed therefore in which the completeness of cobalt removal was determined as a function of standing time. The effect of heating the solution was also examined. In these experiments an accurately measured aliquot of cobalt nitrate solution, containing 5 mg Co, was added to a solution of AnalaR nickel nitrate ($< 0.0005\%$ Co) containing 10 g Ni. The standard separation procedures, as given in the above references, were then used to precipitate cobalt as potassium cobaltinitrite. After measured time intervals the precipitates were filtered, washed, dissolved in 20 ml 6 N H_2SO_4 and made up to 50 ml in standard flasks. These samples were analyzed colorimetrically by the method of YOUNG AND HALL[7] at 625 mμ with a Unicam SP 500 spectrophotometer. The results obtained are given in Table I.

TABLE I

TIME DEPENDANCE OF PRECIPITATION IN COBALTINITRITE SEPARATION

Standing time (min)	*Cobalt recovery*	
	Hot solution (%)	*Cold solution (%)*
10	—	86.27
10	—	85.29
15	50.98	98.63
15	37·25	97·65
30	41.18	98.63
30	75·49	99.02
45	85.88	99.61
45	93·14	99.61
60	88.23	—
60	94·71	—

These results clearly indicate that the cobaltinitrite method meets the requirements of the nuclear physics problem very satisfactorily, provided a standing time of about 45 min is used and the precipitating solution is not heated. It is also indicated that for many analytical applications longer standing times are unnecessary.

The method modified in this manner was successfully applied to the determination of relative nuclear reaction yields described in the second paragraph. Standard carrier techniques were used and the percentage recovery of carrier determined in each precipitation. The reproducibility of the procedure can be inferred from the fact that $> 99\%$ recovery was obtained in all cases. Although the cobalt was precipitated only once, contamination by radioactive nickel was quite small and in any case is rendered negligible by the scintillation spectrometric technique of analysis.

SUMMARY

A reinvestigation of the classical cobaltinitrite method for the separation of cobalt from nickel has shown that the standing time can be reduced to less than 60 min with $> 99\%$ recovery. The method is suitable for the separation of some of the short lived cobalt isotopes.

RÉSUMÉ

Les auteurs ont repris la méthode classique au cobaltinitrite pour la séparation du cobalt d'avec le nickel. Ce procédé peut être utilisé pour la séparation d'isotopes du cobalt de courtes périodes.

ZUSAMMENFASSUNG

Eine neue Untersuchung der klassischen Kobaltnitritmethode zur Trennung von Kobalt und Nickel wird beschrieben. Durch die erzielte Zeitersparniss eignet sich die Methode zur Trennung kurzlebiger Kobalt-Isotope.

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AREA EFFECTS IN ALUMINUM ELECTRODES

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Baker and Morrison[1] reported the observation of a current in a short-circuited cell consisting of an aluminum and a platinum electrode in 0.2 *N* acetic acid. Baker[2] later applied this electrode system to the determination of microgram quantities of fluoride in fuming nitric acid. Repetition of the Baker and Morrison work in this laboratory led to the observation that the magnitudes of current and potential were affected by the area of the aluminum electrode. This observation led in turn to the prediction that a cell consisting of two aluminum electrodes of different areas would develop potential and current. The only comparable observation is a report by Greene and Fontana[3], made after the completion of the experimental work reported here, that a potential and a current develop between a small "artificial pit" and a larger area of stainless steel.

This paper describes experiments that establish the reality of the observation, that define factors controlling the magnitude of current and that establish the framework of the probable electrode mechanism.

Preliminary attempts to repeat the Baker and Morrison work by Holland[4] resulted in current–time curves in which a current nearly constant for as much as one hour was obtained in contrast to the peak-shaped curve of Baker and Morrison. After the area effect was realized in the present work and the areas of the electrodes controlled, the current–time curves could be duplicated.

Use of the rotating aluminum electrode for measurement of fluoride or elements that react with fluoride has been reported by Howard, Weber and Weber[5], Johannesson[6], Kabanov and Polyak[7], Kolthoff and Sambucetti[8] and by Ovsepyan and Tarsyan[9].

EXPERIMENTS ON REALITY OF OBSERVATION

Original observation of area effect

Initial work was done with electrodes made from several turns of No. 14 gauge aluminum mounted in sealing wax. Electrodes with surface areas 2.8 and 1.8 cm^2 gave a potential difference of 18 mV and a current of 2.5 μA when wire electrodes shown in Fig. 1 were placed in 0.2 *N* acetic acid and shorted through a microammeter. Upon addition of 20 μg of fluoride as NaF to 35 ml of electrolyte the current increased to 14.3 mA and the potential to 35 mV.

Effect of impurities in aluminum

Aluminum of 99.0, 99.9 and 99.9999% purity was used to prepare pairs of electrodes similar in areas to those first used. No detectable difference could be found with metal of different degrees of purity.

Effect of shape of electrodes

Pairs of aluminum electrodes with areas similar to those originally used but spherical in shape were used and found to give currents of magnitude similar to those obtained with wire electrodes. Pairs of disc-shaped electrodes shown in Fig. 1 were also prepared from aluminum plate with areas corresponding to those of the original wire electrodes. One face and all corners and edges were coated with Kronig's "cement". The bare faces were exposed vertically, facing upward and facing downward. Again the currents were of similar magnitude.

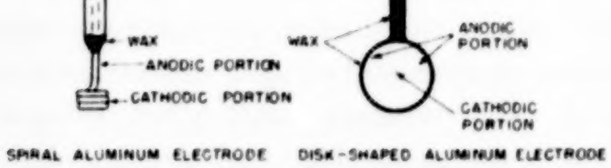

Fig. 1. Wire spiral and disk aluminum electrodes.

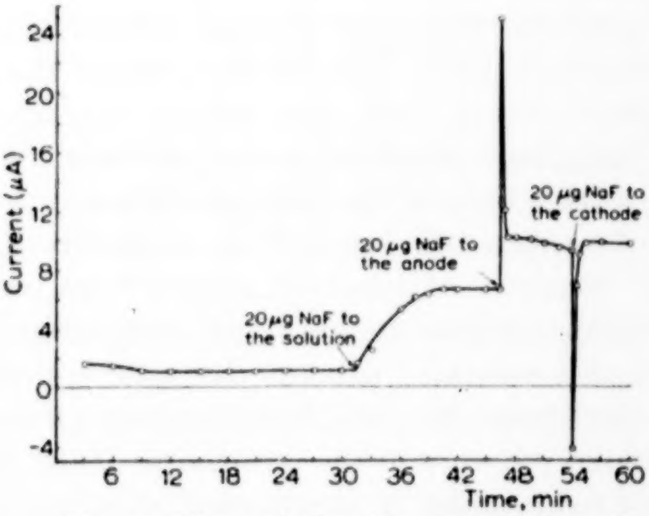

Fig. 2. Effect of fluoride on polarity of aluminum electrode.

Effect of size reversal

The behavior of the current was next studied as the larger electrode was progressively reduced until it was the smaller. The magnitude of the current decreased to zero when the electrode areas were equal. As the area was further reduced, the polarity reversed and the magnitude of the current increased.

Polarity and electrode size

It was observed that the smaller electrode was always the anode. It was found possible to contribute temporary anodic character to the larger electrode by directing a few μg of fluoride against the surface of the large electrode. Fig. 2 shows the changes in current and temporary reversal of polarity when fluoride is directed against the large or small electrode and when it is present in uniform concentration. The reversal of polarity of the larger cathode to anodic character is definite but of only short duration and is convincing evidence for the reality of the anodic character of the smaller electrode in uniform fluoride solution.

EXPERIMENTS INDICATING AN OXIDE LAYER MECHANISM

Effect of strong oxidation and reduction of surface

During the prior experiments, the aluminum metal used for electrodes was in equilibrium with the air. Some variation in currents had been noted after the same piece of metal had received different treatments of washing and drying. This suggested the probability of an oxide layer being present and its involvement in the mechanism.

Aluminum electrodes were therefore oxidized by heating to 275° in air for 2 h. The treatment resulted in the complete desensitizing of the electrode to fluoride. Only after extensive treatment in hydrofluoric acid was the sensitivity restored. Similarly treatment with hydrogen at 400° also completely desensitized the electrode. However, upon standing in air at room temperature for periods up to 1 h, the sensitivity was restored. These experiments indicate the probable participation of an oxide layer in the reaction. They also indicate that an optimum thickness of oxide is needed and that this is obtained in a reproducible way by ample exposure to air. The absence of sensitivity in the highly oxidized surface appears to result from the development of a substantial layer of less conductive oxide.

Removal of dissolved oxygen from the electrolyte increased the current by 10% when a cell consisting of an air-equilibrated aluminum electrode, 0.2 N acetic acid and a saturated calomel electrode was shorted. When the aluminum electrode was inactivated by reduction in hydrogen, the presence of dissolved oxygen caused a more rapid recovery of the sensitivity. If the electrode were precoated with a heavy layer of oxide and thus inactivated, dissolved oxygen in the electrolyte had no noticeable effect upon the recovery of sensitivity.

Dependence of sensitivity upon pH

Since an oxide layer appeared to be involved on the aluminum surface, it was expected that the electrode would be responsive to changes in pH. Fig. 3 shows the current response due to 20 μg of fluoride in solutions of pH 2–6 prepared from mixtures of acetic acid and sodium acetate. Current response is maximum near pH 3.4. It should be noted that the pH value, 4, at which the current decreases markedly is about the pH of incipient precipitation of $Al(OH)_3$. Current decrease in both acid and alkaline directions may be due to removal of the oxide film by either hydrogen or hydroxyl ions. The result is then comparable to the decrease in current noted after strong reduction of the electrode in hydrogen gas at 400°. Both experiments indicate an optimum thickness of oxide for maximum current response.

Effect of ultrasonic vibration

On the basis that previous experiments indicate a layer of oxide is involved in the electrode mechanism, that an optimum thickness is needed for maximum current response and on the basis of the probability that ultrasonic energy could either disturb or remove the oxide layer, the electrodes were placed in a plastic cell immersed in the bath of an ultrasonic generator whose characteristics were 30–35 kilocycles, 0.9 kV and 200–204 mA. With the cell operating and a current of 4.0 μA flowing, the ultrasonic generator was turned on. Immediately the current dropped to ± 0.2 μA shown in Fig. 4. When the ultrasonic energy was discontinued, the current returned to its original value in 5–10 min.

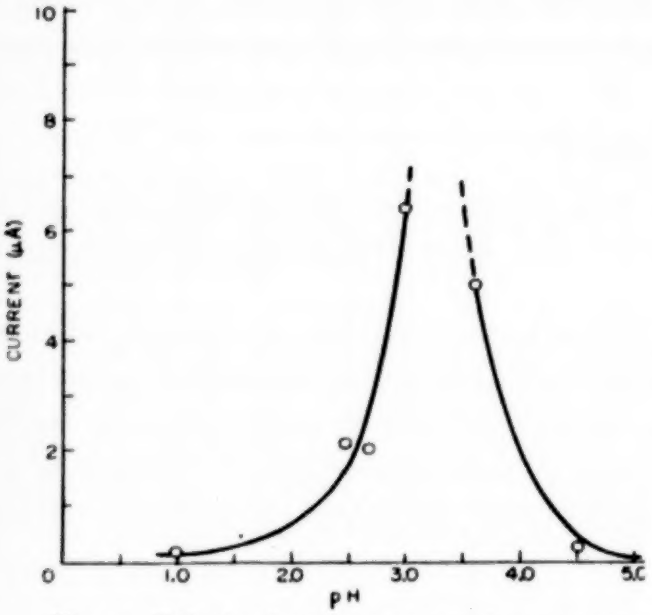

Fig. 3. Effect of pH on current response to 20 μg of fluoride.

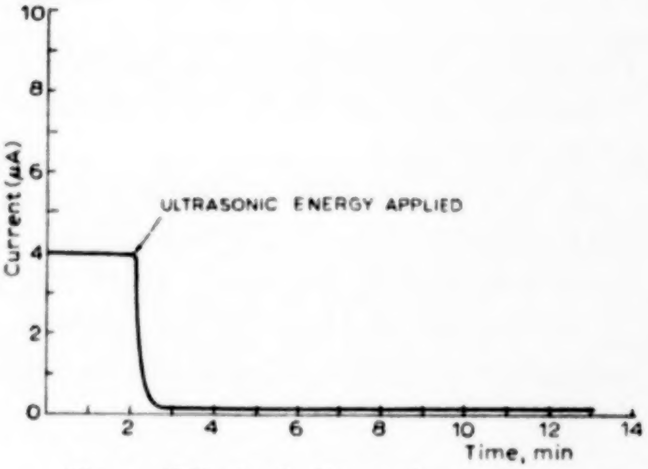

Fig. 4. Effect of ultrasonic energy upon current response.

During the work it was found that a minimum intensity of ultrasonic energy is needed before any effect is observed. The energy required seems critical since the destructive effect upon the current was immediate and complete, once the minimum effective energy was reached.

EXPERIMENTS ON LOCALIZED POLARIZATION

Microscopic observation of surfaces

Inspection of the spiral electrode showed pitting on the upper portion of the wire. Disk-shaped electrodes coated with wax on one side and on the edge were also found to develop pits near the wax-metal interface. The pits were deeper toward the circumference of the disk.

Exploration of the surface of a disk-shape electrode with a Luggin capillary showed that the metal near the circumference was consistently 8–10 mV more negative than at the center. Since the pits on the wire electrodes were more prominent toward the top, it is concluded that a potential difference also exists between the top of the electrode and the coils; that the top is anodic with respect to the coils; that when the number of coils is changed the top anodic area remains constant while the cathodic coil area changes. Thus in the early experiments in which the size of wire electrodes was changed, the anodic areas of each electrode remained constant and only the cathodic areas were different.

Little difference in behavior could be found by changing the composition of the wax, KRONIG "cement", to ordinary red sealing wax. However, when the wax was omitted and experiments repeated with bare aluminum electrodes of different areas, the magnitude of the current decreased by about one-fifth that observed when a wax-metal interface was present.

Electrodes were also coated with Duco lacquer, glue, styrene resin, and soft glass. In all cases they gave larger currents than bare electrodes of essentially the same areas.

DISCUSSION

The effects of a difference in cathode area or a reduction of the cathode area can be considered equivalent to three circumstances that arise during the electro-chemical action of a cell.

(*1*) A reduction of the cathode size is equivalent to the reduction of the electrode area of an ordinary cell. (*2*) The reduction of the cathode area can be considered comparable to enlargement of the anode. In either, the ratio of cathode to anode areas decreases. (*3*) Reduction of the effective cathode area is also accomplished by increasing the number of corrosion pit sites on the cathode. Such area reduction increases the current density.

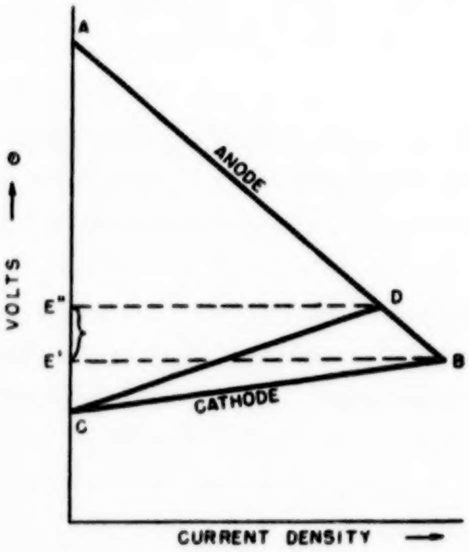

Fig. 5. Corrosion polarization diagram for two electrodes of different area.

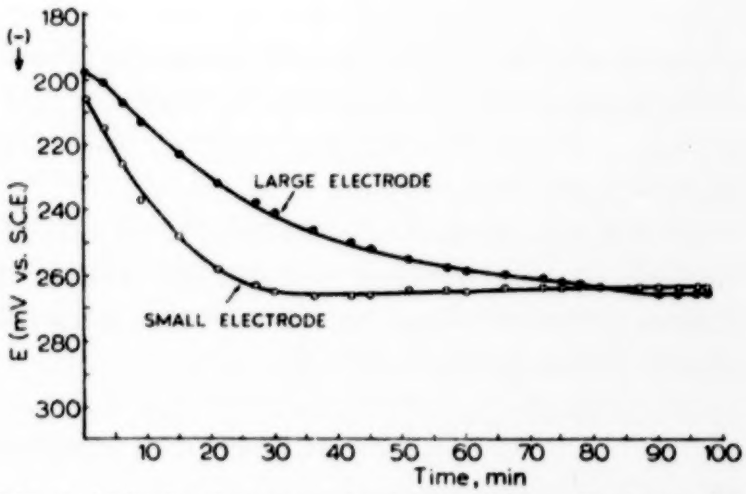

Fig. 6. Polarization rates for large and small electrodes in non-flowing electrolyte.

The effect of reducing the cathode size is shown in the instantaneous polarization diagram, Fig. 5. This is a corrosion polarization diagram and not an impressed current polarization diagram. The diagram shown in Fig. 5 is for a cell known to be anodically controlled such as in the dissolution of aluminum. Line ADB represents the anode potential and lines CB and CD the cathode potentials for two different cathode areas. In such a diagram, changes in potential and current density of an electrode are represented by a change in slope of the corresponding potential line, for example CB and CD of the diagram.

Consider two cells, one represented as ABC with a corrosion potential of E^1. The cell with the smaller cathode has the more negative potential and thus is anodic with respect to the larger cell. The difference in potential between the two cells $= E^1 - E^2$.

The effect of the difference in electrode sizes of two aluminum electrodes in producing a potential is understandable in terms of the corrosion polarization diagram in Fig. 5. Both anodic and cathodic sites exist on each electrode. The anodic areas are equal and only the cathodic area changes. The potential of the cell is the difference between the net effects for each electrode.

Throughout the experiments with two aluminum electrodes, it was observed that in a static system (stirred, but non-flowing) the current rose rapidly to a maximum and then decreased asymptotically. The potential of each aluminum electrode of a 3 : 1 area pair was therefore measured individually against a calomel electrode as a function of time. Fig. 6 shows that the difference in potential between the large and small electrode exhibits a maximum in 20–25 min. This behavior corresponds to the appearance of maximum currents.

The eventual coincidence of the potential–time curves for a large and a small electrode in the same solution (Fig. 6) is convincing evidence of a differential polarization effect on the large and small electrodes during the early stages of current passage. Obviously both surfaces approach equality after most of the fluoride has been removed from the electrolyte. The constancy of the current observed with a flowing electrolyte containing fluoride is attributed to a constant rate of removal of fluoride at the aluminum electrode surface.

SUMMARY

Potential differences and current flow have been observed between two aluminum electrodes of different sizes (areas) in solutions of dilute acetic acid containing small amounts of fluoride. The smaller electrode is regularly the anode. Reduction of the size of the larger electrode until it is the smaller reverses the polarity. Impurities and geometric shape of the electrodes have no detectable influence. Extensive oxidation, reduction and exposure to ultrasonic energy desensitize the electrode function. Air-equilibrated surfaces show a maximum response. Dissolved oxygen in the electrolyte has a small damping effect upon the response. Sensitivity is greatest in the pH range 2.5–4.5. Each electrode is found to have non-uniform distribution of potential and is more anodic in regions adjacent to surface coatings of wax, etc. Dependence of a mechanism upon participation of the oxide layer is indicated.

RÉSUMÉ

On a observé des différences de potentiel et de courant entre deux électrodes d'aluminium de dimensions variables dans des solutions diluées d'acide acétique contenant de faibles quantités de fluorures. La plus petite des électrodes est régulièrement l'anode. En réduisant la dimension de la plus grande jusqu'à ce qu'elle devienne la plus petite, on renverse la polarité.

ZUSAMMENFASSUNG

Spannungsunterschiede und das Fliessen von Elektrizität wurden beobachtet zwischen zwei Aluminiumelektrode von verschiedener Grösse (Oberfläche) in kleine Mengen von Fluorid enthaltenden Lösungen von verdünnter Essigsäure. Die kleinere Elektrode ist gewöhnlich die Anode. Verkleinerung des grösseren Elektrode zur kleineren andert die Polarität.

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REVUES DE LIVRE

Instability Constants of Complex Compounds par K. B. Yatsimirskii et V. P. Vasil'ev, Pergamon Press, London, 1960, 218 p., Prix: 42 s.

Le nombre des travaux publiés dans ce domaine est considérable et les méthodes utilisées pour la détermination de la constante des complexes fort nombreuses, si bien qu'il est souvent difficile de s'y retrouver. Les auteurs de cet ouvrage ont donc fait oeuvre utile et le remarquable travail de synthèse qu'ils ont entrepris sera apprécié des chimistes. Dans une première partie, les auteurs se sont attachés à définir les termes utilisés dans le domaine des complexes successifs, à décrire leur comportement en solution et leurs propriétés. Dans un 2ème chapitre, ils présentent de façon fort claire les différentes méthodes proposées pour la détermination des constantes, qu'ils classent en deux groupes.

Le groupe I comprend les méthodes basées sur l'étude des équilibres hétérogènes, les méthodes électrométriques.

Le groupe II comprend la méthode spectrophotométrique, la méthode par conductivité électrique et celle basée sur la cryoscopie.

Un troisième chapitre traite des conditions thermodynamiques de formation des complexes en solution et le suivant, des facteurs ayant un effet sur la stabilité des complexes.

Enfin, l'ouvrage se termine par une vaste table donnant les constantes d'instabilité des 1381 complexes. La bibliographie va jusqu'en 1954 et pour certains d'entre eux jusqu'en 1956. Le tout est accompagné de nombreuses références bibliographiques. Ces mises au point sont extrêment précieuses car les chimistes de notre temps ne peuvent suivre les progrès de leur science que si on met à leur disposition — c'est le cas pour cet ouvrage — des exposés dépouillés de tout ce qui n'est pas indispensable, une sorte de résumé clair, ordonné, conçu dans un esprit de synthèse.

Le rôle joué par les complexes en chimie analytique est de plus en plus important, tant dans les processus de séparation que dans les dosages chimiques et physicochimiques.

Le livre que nous présentons sera donc un auxiliaire précieux pour tous les analystes.

D. Monnier (Genève)

Anal. Chim. Acta, 23 (1960) 396

Proceedings of the International Symposium on Microchemistry held at Birmingham University, Sponsored by the Society for Analytical Chemistry, XXVI + 583 p., Pergamon Press, London, 1960, 100s.

C'est avec un grand plaisir que nous annonçons aujourd'hui la parution des comptes rendus du Congrès de Microchimie, tenu à Birmingham du 20 au 27 août 1958.

Le volume que nous avons en mains comprend les 60 communications faites à cette occasion par des savants de 25 pays différents, ainsi que les discussions ayant suivi chaque exposé scientifique.

L'intérêt que suscite ce livre est évident. Le lecteur y trouvera un grand nombre de nouvelles méthodes microchimiques, mises au point par des spécialistes dont les noms dépassent largement les frontières de leurs pays; il sera ainsi amplement orienté sur les tendances modernes de la microchimie.

Vu le nombre important des communications, nous ne pouvons en donner ici les titres. Nous tenons pourtant à signaler qu'elles couvrent les domaines suivants:

Microanalyse qualitative (4 communications), minéralisation des matières organiques (2), pesée (2), dosage des éléments et des groupes (11), détermination des constantes physiques (1), méthodes biochimiques (3), chromatographie et échange d'ions (4), polarographie (5), méthodes radiochimiques (4), méthodes spectrochimiques (6), titrimétrie (6), complexométrie (5), applications industrielles de la microchimie (3), enseignement (3), appareillage (1), contribution de la Grande Bretagne au progrès de la microchimie (1).

La présentation du livre est impeccable. Nous regrettons qu'il soit paru avec quelque retard, quoique cela ne change rien à sa valeur, et nous le recommandons vivement à tous les chimistes qui désirent se tenir au courant des progrès récents de la microchimie en général.

I. Kapetanidis (Genève)

Anal. Chim. Acta, 23 (1960) 396

THE DETERMINATION OF VANADIUM IN ROCKS AND METEORITES BY NEUTRON-ACTIVATION ANALYSIS*

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Atomic Energy Research Establishment, Harwell (Great Britain)

(Received May 23rd, 1960)

INTRODUCTION

The determination of vanadium in geological material has up to now depended almost entirely on spectrographic methods. With modern techniques the sensitivity of this method for vanadium is 3 p.p.m.[2]. However, the results reported by different analysts on the same material vary greatly as will be evident from an inspection of the analytical results for G-1 and W-1 (see Table II). Furthermore, as a result of a vanadium–calcium spectral line coincidence at 3185 Å (which was used for vanadium determinations by some workers) it was recently[3] stated that the vanadium contents of G-1 and W-1 are not at all well known.

An independent method for determining vanadium in geological material would serve the useful purpose of checking the spectrographic results. A method with increased sensitivity would be desirable if determinations below the 5 p.p.m. level are to be made with a reasonable degree of precision.

Neutron activation analysis is a technique that is applicable to the determination of many trace elements. It has been used for the determination of vanadium in a number of materials. However, the relatively short half life of the vanadium isotope formed on neutron-activation (3.76 min ^{52}V), restricted the activation method to those materials where chemical separation is not necessary, *i.e.* where the determination could be carried out entirely by instrumental means. SMALES AND MAPPER[4] determined vanadium in graphite, BROOKSBANK *et al.* in crude oils[5] and titanium[6], LELIAERT *et al.* in high alloy steels[7]. Recently MEINKE[8] determined vanadium in biological ash by a simple separation followed by γ-spectrometry. No general application in geochemistry has been reported up to now, and the neutron-activation technique has been chosen for this work.

Feasibility of the neutron-activation method

On bombardment of natural vanadium with slow neutrons, only one radioactive isotope is formed by the (n, γ) reaction. The nuclear characteristics of the nuclides involved are as follows (see Table I).

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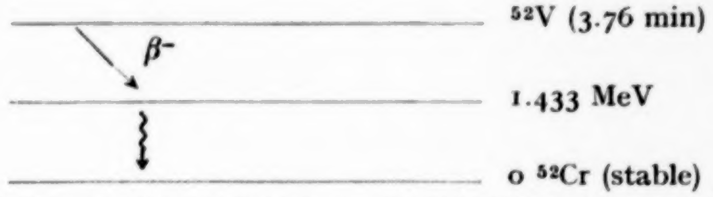
* This paper has been reproduced previously as a U.K.A.E.A. report[1]. It is presented here in a slightly modified form.

TABLE I

NUCLEAR DATA OF VANADIUM

Target nuclide	*Abundance in natural element, %*	*Isotopic activations cross-section, barns*	*Product of neutron-irradiation*	*Radiation and energy MeV*		*Half life of product nuclide*
$^{51}_{23}V$	99.75	4.5	$^{52}_{23}V$	β^- γ	2.5 1.433	3.76 min

Decay scheme of ^{52}V:



It can be calculated[9] that on irradiation to saturation in a flux of 10^{12} neutrons per sq. cm per second, 1 μg of vanadium will give $3.17 \cdot 10^6$ disintegrations/min. On the assumption of 10% detecting efficiency, this means $3.17 \cdot 10^5$ counts/min at the end of irradiation. Ten half lives (*i.e.* 37.5 min) after the end of irradiation, approximately 300 counts/min will be recorded under these conditions. Because of the relatively short half life involved, good statistical accuracy cannot be obtained at this level of activity, which means that separation will have to be completed several half lives before this time. Assuming a count rate after separation, of at least 1000 counts/min for reasonable statistics, separation must be completed by not later than about eight half lives (*i.e.* 28 min) after the end of irradiation of 1 μg vanadium. The actual time available will be shorter than this, as in this calculation a 100% chemical yield was assumed. At lower levels of vanadium the separation time will have to be decreased accordingly (*e.g.* at the 0.1-μg level the above count rate will be reached about 5 half lives, *i.e.* about 18 min after the end of irradiation).

EXPERIMENTAL

The "rabbit"

For rapid transfer of the irradiated samples from the pile to the laboratory, the pneumatic "rabbit" device was found to be most useful, as the samples are actually delivered in the building where the analysis was carried out. The "rabbit" was used for irradiations throughout this work. Under normal conditions it was possible to begin separation on the irradiated samples 3 to 3.5 min after it had left the pile.

The neutron flux distribution in the "rabbit" position was not known and had to be determined. This was done in the following way: A 7 × 7 mm perspex bar was cut to fit tightly inside the "rabbit" along its length. Twelve pieces of specpure cobalt wire approximately 3 mm long and of known weight, were taped with sellotape at regular intervals along the length of the perspex bar. This was then fixed inside the "rabbit" (Fig. 2a) and irradiated for 15 min in the "rabbit" position. After irradiation sufficient time was allowed for the 10.5-min isomer of ^{60}Co to decay away. Each piece of wire was then taped to the centre of an aluminium counting tray, γ-counted on a sodium iodide thallium activated scintillation counter and the specific activity in each case calculated. Sufficient count time was allowed to record at least 10^5 counts on each sample.

The results of this experiment are shown graphically in Fig. 1. The shape of the distribution curve shows a reasonably constant flux along the length of the top half of the "rabbit" and a rapid decrease to the extent of about 10% along the bottom half. In a separate experiment the radial distribution was found to vary by not more than 1 to 2%, so that this could be neglected.

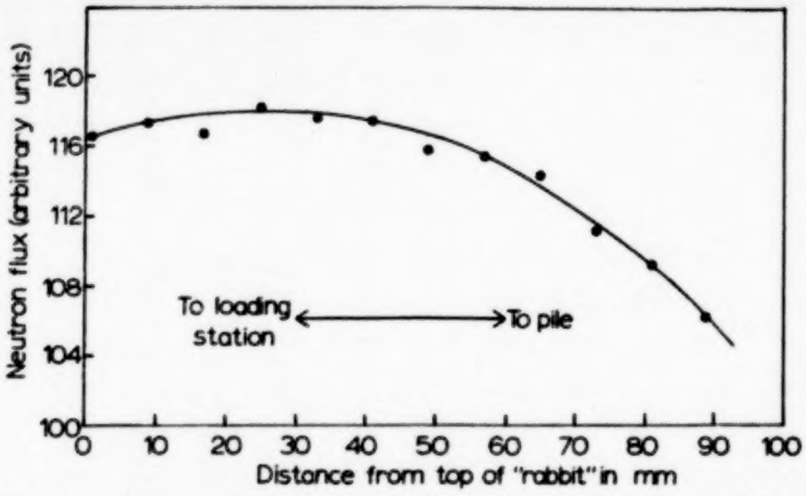


Fig. 1. Neutron flux distribution in the "rabbit" position.

Thus, to obtain the maximum neutron flux and to ensure the same uniform flux through both sample and standard, it is advisable to confine the specimens to be irradiated to the top half of the "rabbit".

Irradiation

The samples for analysis were already ground to 100 or 200 mesh. A suitable quantity (25 to 230 mg) was weighed into a dry silica ampoule of 4 to 6 mm internal diameter with a constriction at not more than 45 mm from the closed end. It was then sealed off at the constriction, taking care first to make another constriction about 10 mm from this end. This greatly facilitated cutting after irradiation. A suitable quantity of dilute aqueous standard solution (25 to 150 mg) was weighed into an identical silica ampoule and sealed off at the constriction. The two ampoules were packed side-by-side in a polythene container with a tight fitting cap and fixed tightly between the cap and a plug of paper tissue in the bottom. The container was then packed in the "rabbit" with sufficient paper tissue in the bottom to fix it firmly in the top half of the "rabbit" after the lid has been screwed on (see Fig. 2B).

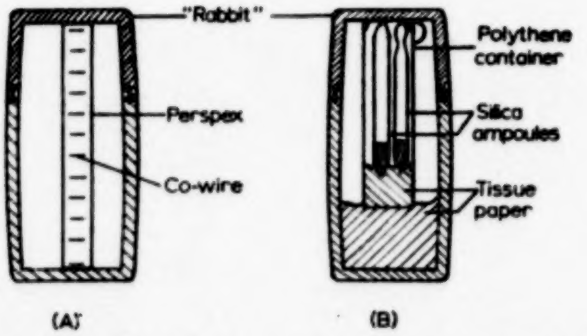


Fig. 2. Packing of samples in "rabbit" for: (A) determination of neutron flux distribution, (B) determination of vanadium.

The whole assembly was then irradiated in the Harwell Pile, BEPO, for a predetermined time which ranged from 10 sec to 15 min for the various samples analysed.

Chemical separation

No radiochemical methods have been reported for separation and purification of vanadium activity from irradiated rock- or meteorite-samples. Preliminary experiments indicated that, after the vanadium activity has been separated from the bulk of the major constituents of rock samples, it could be readily purified in most cases by solvent extraction. The method finally adopted permitted the vanadium activity for both sample and standard to be measured 13 to 14 min after the sample has left the pile. This means that the actual separation time was of the order of 10 to 11 min.

This separation consists of rapid dissolution of the sample by sodium peroxide fusion, followed by a series of extractions of the vanadium as the cupferron complex with chloroform in presence of EDTA as masking agent. Under proper conditions this gave adequate radiochemical purity for most samples. Chemical interference was caused in some cases by molybdenum, due to 14-min ^{101}Mo. The extent of this interference depends on the molybdenum content of the sample and the irradiation time, which is in turn determined by the vanadium content. In the samples analysed this interference was encountered in all cases where the vanadium content was less than about 15 p.p.m.

The molybdenum activity could be easily removed by ether extraction of the chloride without sacrificing too much time. However, the decay product of ^{101}Mo, ^{101}Tc, proved to be troublesome and could not be removed completely within a reasonable time. This difficulty was finally overcome by resolution of the composite decay curve obtained in these cases, after the decay of the technetium had been followed until background level was reached.

Measurement of radio-activity

The final chloroform-extract of vanadium was transferred to an M6H type liquid counter and counted with a dekatron type scaler. Two separate counting systems were used, one for the standard and one for the sample. Rack mounting of the scalers, one above the other, permitted the two count switches to be operated simultaneously by coupling them together with a piece of wire. It was found fairly easy to select two tubes working on the same voltage and this permitted the use of only one E.H.T. unit. A block diagram of the complete system is shown in Fig. 3. Investigation of

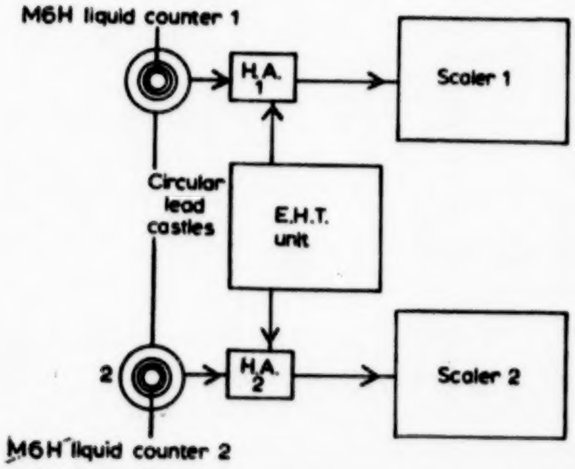


Fig. 3. Block diagram of counting equipment.

the characteristics of a counter of this type led to the tubes being used in a rather unusual way.

If an active solution is added ml by ml to one of these tubes and the count rate determined after each addition, it is found that the total count rate increases rapidly until a volume of 7 to 8 ml is reached. Further addition of active solution results in a rather slow increase in total count rate until finally it remains practically constant with further additions beyond about 10 ml. If now the specific activity of the solution in counts per min per ml is plotted against the volume of solution added, a curve like those shown in Fig. 4 is obtained. The curves in this figure are for two different tubes.

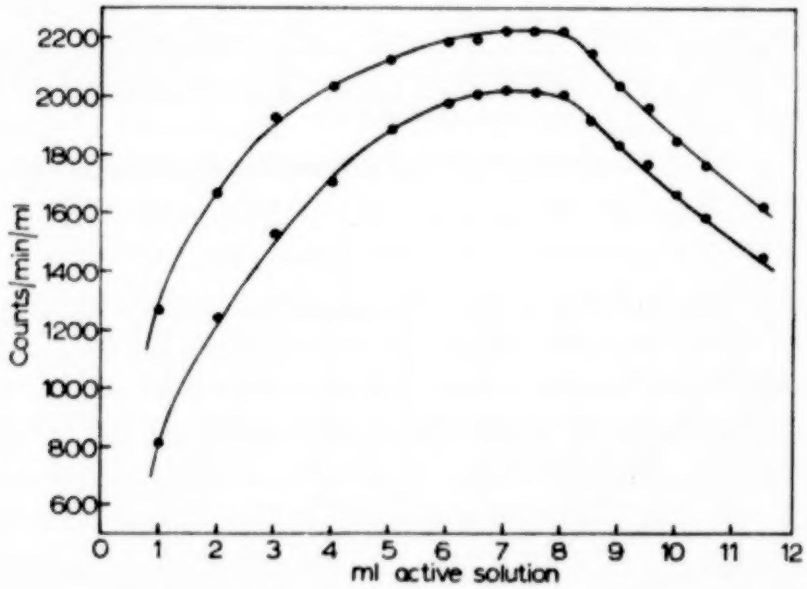


Fig. 4. Variation of specific activity with volume for two M6H type liquid counters.

The general shape of these curves shows a broad maximum from about 6 to 8 ml over which the specific activity remains practically constant. By using the tubes over this region the bulk of the vanadium activity could be transferred to the detector and counted with maximum sensitivity.

By performing the final extraction with about 8.5 ml chloroform, a volume of about 7 ml was usually obtained after separation of the phases and filtration. This was then transferred directly to the tubes and the decay of the vanadium followed in the following way.

Wherever possible quantity of sample (and standard) and irradiation time were so chosen so as to record, after separation, 10,000 to 15,000 counts/min. This was, of course, not always possible. Indeed, at the 0.1 p.p.m. level in rocks, only a few hundred counts/min total activity were normally recorded. Counting begun at any convenient time as shown on a stopwatch which was started as soon as the "rabbit" left the pile.

1-min counts were then made for both sample and standard simultaneously with $^1/_4$-min intervals between counts. This was necessary in order to record the number of counts and time for both. When the count rate for any one of the sample or standard had dropped to less than 10,000 counts/min, the count time was gradually increased to keep the total number of recorded counts, during each count time, of

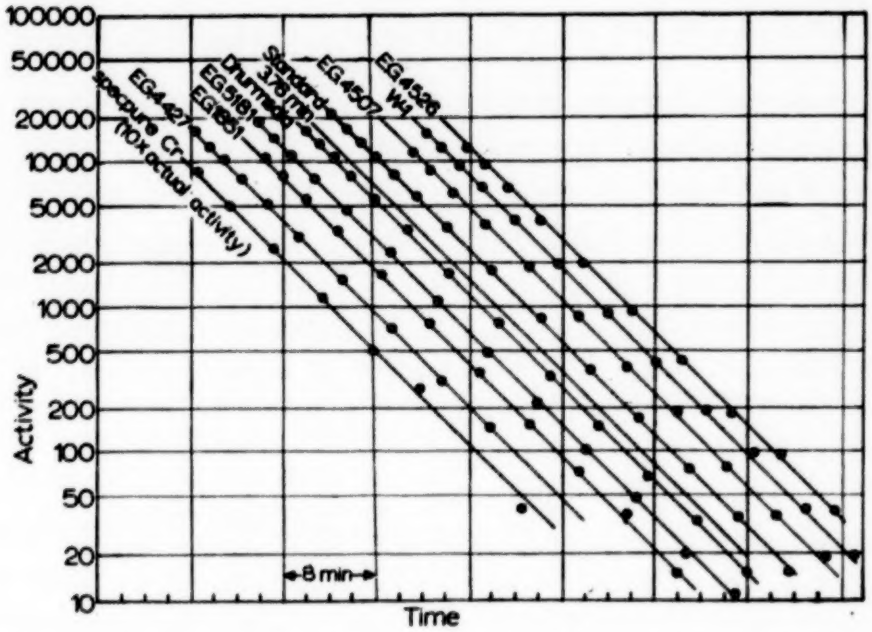


Fig. 5. (a) Decay curves for ^{52}V separated from various samples.

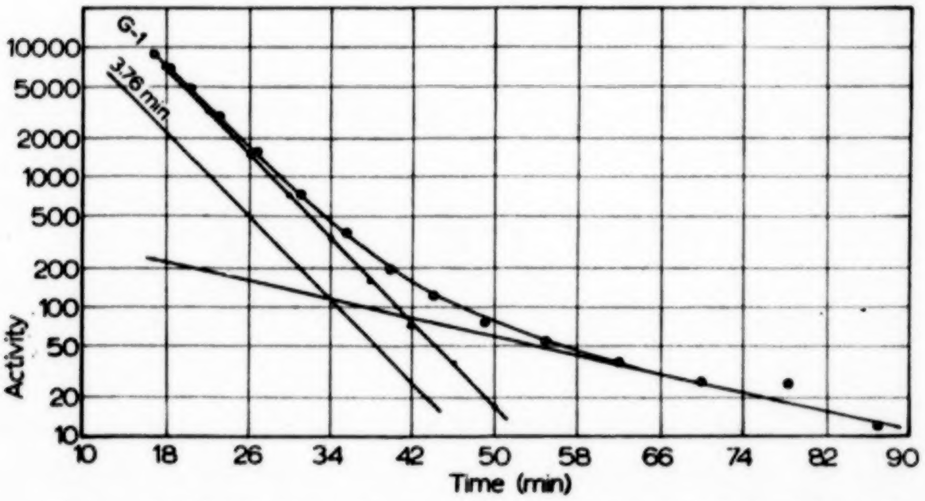


Fig. 5. (b) Resolution of composite decay curve obtained from G-1.

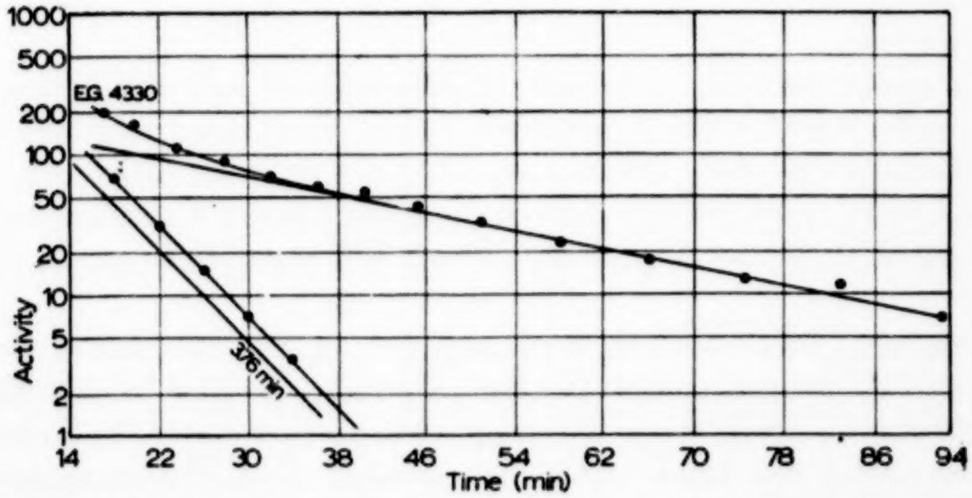


Fig. 5. (c) Resolution of composite decay curve obtained from E.G. 4330.

the order of 10,000. However, counts lasting more than 4 min were normally not made, as this is already long compared with the half life involved. This procedure normally resulted in the following count times: 1.0, ... , 1.5. 2.0, 3.0, 4.0, 4.0 . . . . etc. min; (with low activity samples 2- or 3-min counts were made at the beginning).

The decay was followed in this way for about seven half lives and decay curves constructed after suitable corrections for paralysis losses and background had been made. For this purpose the number of counts per unit time, calculated from the total number of counts recorded over a certain time, was assumed to be equal to the activity at the midpoint of the duration of count.

In this way it was found that the experimental points (for both standard and sample) always lay on a straight line parallel to the theoretical decay line for ^{52}V of 3.76 min. This confirmed the radiochemical purity of the isolated vanadium. Fig. 5A shows the experimental lines obtained for a number of samples and standards together with a theoretical line of 3.76-min half life. Also shown is the composite curve obtained in presence of ^{101}Tc interference and the resulting resolution of this curve for two different samples (Figs. 5b and c).

The efficiency of the two counting systems was not the same and had to be determined. Before this was done, the paralysis time of both head amplifiers was adjusted to 400 μsec. This ensured that practically the same count rate was observed when the same sample was counted with the same liquid tube on both counting systems. Any difference in count rate with different tubes connected to the two systems was then almost entirely due to differences in efficiency of the two tubes. About 14 ml of an active solution of vanadium–cupferrate in chloroform was prepared and after transferring about 7 ml to each one of two liquid counter tubes, the decay was followed as described above. After chemical yield determination (see below) the relative efficiency, and thus the efficiency correction factor, could be calculated. This determination was made at frequent intervals during the course of this work and could always be reproduced to within 2%. Alternating the sample between the two counting systems in successive determinations on the same sample served as a further check on this.

Calculation of vanadium content

The ratio of count rate of sample to count rate of standard was calculated for the first few experimental points where statistics were reasonable and the mean of these values determined. After suitable efficiency correction, this ratio was used to calculate the vanadium content of the sample. In cases where resolution of the decay curve was necessary, this ratio was determined from the resulting decay line.

Chemical yield determination

After counting on a sample (and standard) was completed, the solution was quantitatively transferred to a 25-ml volumetric flask by means of chloroform from a polythene wash bottle. After dilution to the mark and mixing, the solution was left for at least 20 min (see below). Relative chemical yields were then determined colorimetrically with the Spekker colorimeter using 1-cm cells and distilled water as the reference solution.

For calculation purposes the reading obtained on the colorimeter drum was used as a direct measure of the chemical yield. This was found to be permissible under proper experimental conditions which were determined as follows: A series of solutions containing increasing concentrations of vanadium as the cupferrate in chloroform was prepared. After allowing sufficient time for stability to be reached (see below) the absorption of each solution was measured. The results, shown graphically in Fig. 6, indicate a linear relationship up to a drum reading of 0.55. By using initially 5 mg vanadium carrier and diluting the final extract to 25.0 ml in a volumetric flask, the chemical yield for both sample and standard is confined to within this limit.

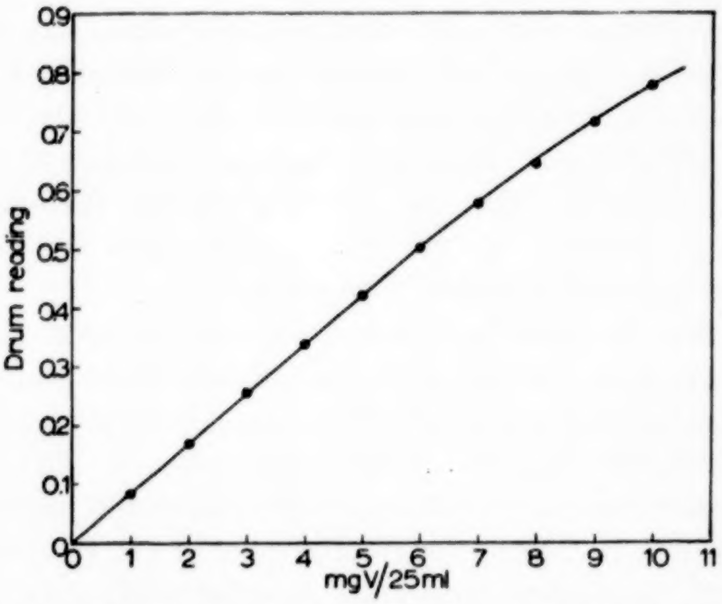


Fig. 6. Variation of optical density of vanadium-cupferrate in chloroform with concentration.

Upon dilution of the vanadium–cupferrate with chloroform, the brown colour fades rapidly to a yellowish-brown or yellow depending on the concentration. A freshly prepared solution containing about 8 mg vanadium as the cupferrate in 100 ml chloroform reached stability after 15 to 20 min, after which it was stable for several hours.

The chemical yield usually varied between 25 to 40% for the samples and 50 to 60% for the standards.

METHOD

Reagents:

Standard vanadium solutions: A solution containing 1 mg vanadium per ml was prepared by dissolving the appropriate quantity of specpure vanadium pentoxide in ammonia solution. This was acidified with sulphuric acid, quantitatively transferred to a suitable volumetric flask, diluted to the mark and homogeneously mixed. This solution was checked by titration against standard ferrous solution[10].

This stock solution was used to prepare a series of dilute standard solutions by diluting the desired accurately known volumes in a suitable volumetric flask, after a further quantity of sulphuric acid had been added to each. The density of each solution was determined immediately after preparation by weighing 10.0 ml in a stoppered weighing bottle.

Vanadium carrier solution: One litre of a solution containing 1 mg vanadium per ml was prepared by dissolving the appropriate quantity of vanadium pentoxide in sodium hydroxide, neutralizing with sulphuric acid to a pH of 3 to 4, and diluting to the mark in a volumetric flask.

Molybdenum carrier solution: 5 mg molybdenum per ml.
Hydrochloric acid, sp. gr. 1.18; Sulphuric acid, 12 *N*; Sodium hydroxide, 1 *N*; Ammonia solu-

tion, 1 *N*; Potassium permanganate, *ca.* 0.1 *N*; Cupferron solution, 3% in distilled water; Tetraphenyl arsonium chloride, 0.001 *M*; EDTA solution, 5% di-sodium ethylene diaminetetraacetate; Sodium peroxide, powdered.

Procedure

As soon as the "rabbit" leaves the pile at the end of irradiation, a stop watch is started. Upon arrival at the loading station, the polythene container is immediately removed from the "rabbit" and taken to the laboratory as quickly as possible.

The separation of the sample and standard is described separately below.

Sample in absence of Mo-interference

Open the ampoule at the constriction after tapping lightly to ensure that all the sample is in the other end of the tube. Transfer to a 5-ml nickel crucible containing about 2 mg sodium peroxide, mix thoroughly with a small stainless steel spatula and cover the mixture with a thin layer of sodium peroxide. Carefully fuse the mixture by holding the crucible with a metal tong in the flame of a Meker type burner, taking care to prevent splashing as much as possible. As soon as the whole mass is fused, heat to a dull red with continuous swirling of the crucible. Then quench the melt by dipping the lower part of the crucible in cold water. Put the crucible on its side in a 250-ml tall form beaker containing 5 mg vanadium carrier in about 13 ml total volume and cover with a watch glass. As soon as the vigorous reaction subsides, heat to boiling over a Bunsen and continue boiling for about 20 sec. Transfer the contents of the beaker (excepting the crucible) to a 50-ml centrifuge tube, rinsing the beaker and crucible once with water, and centrifuge. Decant the supernate into a 150-ml beaker containing a small block of ice and quickly neutralize with hydrochloric acid, using a glass tube of about 5 ml capacity drawn out at one end and fitted with a rubber bulb at the other end. (The precipitate of silica, etc. which first forms and then dissolves again, and/or the colour change in the solution, serves as a useful indicator). Transfer the clear solution to a 250-ml separating funnel containing 25 ml chloroform, 3 to 5 ml hydrochloric acid and 1 to 2 ml 5% EDTA solution.

Add about 2 ml 3% cupferron solution and extract the vanadium cupferrate into the chloroform. Allow to settle and drain off the organic layer into a 100-ml separating funnel containing about 20 ml 1 *N* ammonia or sodium hydroxide. Back extract the vanadium cupferrate into the aqueous phase by vigorous shaking and discard the organic phase after settling. Add about 8.5 ml chloroform, 10 ml water and 1 to 2 ml EDTA, acidify with hydrochloric acid and re-extract the vanadium cupferrate into the chloroform. Allow to settle, filter the organic phase through a Whatman No. 4 paper into a 10-ml measuring cylinder, collect about 7 ml of the solution, transfer to the liquid counter tube and count as already described. (Purpose of the filtration is to remove any moisture accompanying the chloroform. The precipitate in the centrifuge tube, consisting to a large extent of nickel oxide, was always treated with concentrated hydrochloric acid and left for some time, with occasional shaking. A clear solution usually resulted, indicating complete dissolution of the sample).

Standard

The separation steps for the standard are fitted in between those of the sample in any convenient way. First, drop the standard ampoule into a solution containing vanadate, permanganate and sulphuric acid and leave for a few minutes. This is to remove any possible surface contamination.

Take the ampoule out of the solution, rinse thoroughly with distilled water and drop into a 400-ml polythene beaker containing 5 mg vanadium carrier and 5 to 10 drops of potassium permanganate in a total volume of about 25 ml. Crush the ampoule with an aluminium rod and hammer (see Fig. 7). After rinsing of the rod and inner wall of the beaker, add 2 to 3 ml sulphuric acid and leave until a convenient time for further treatment.

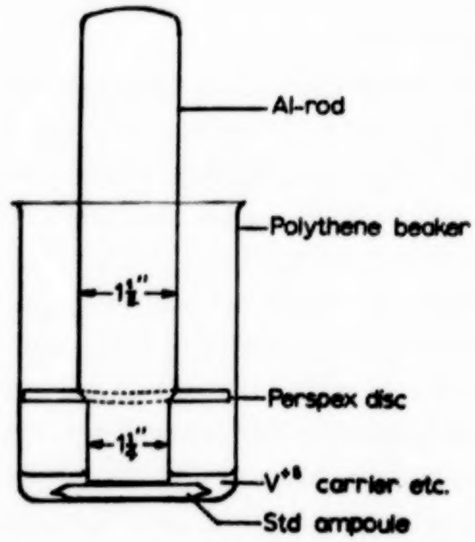


Fig. 7. Apparatus used for crushing of standard ampoules.

Transfer the solution to a 250-ml separating funnel containing 25 ml chloroform, add about 2 ml cupferron solution and extract the vanadium as before. Further treatment of the standard is exactly as described for the sample.

Sample with Mo-interference

The procedure for these samples is exactly the same as that described above up to neutralization of the supernate after centrifugation. Transfer the resulting clear (cold) solution to a 250-ml separating funnel containing 50 ml di-ethyl ether, 15 to 20 ml hydrochloric acid and about 3 mg molybdenum as sodium molybdate solution and extract the molybdenum into the ether layer. After settling, drain off the aqueous layer into a 250-ml separating funnel containing 25 ml chloroform, 120 ml water and 3 or more ml cupferron solution. Extract the vanadium into the chloroform, leave to settle and drain off the organic layer into a 100-ml separating funnel containing 20 ml 1 *N* sodium hydroxide and about 1 ml 0.001 *M* tetraphenyl arsonium chloride. Shake vigorously, settle and discard the organic phase. Acidify the aqueous phase with hydrochloric acid, add about 8.5 to 9 ml chloroform, about 10 ml water and re-extract the vanadium into chloroform. Leave to settle and filter the organic layer into a 10-ml measuring cylinder, collect about 7 ml, add 3 drops methanol, stopper the cylinder and mix thoroughly. Transfer to counting tube and count. (The tetraphenyl arsonium chloride is added in an attempt to remove the $^{101}\mathrm{Tc}^{11}$ but it is not very successful under the present conditions).

Counting is made in the way already described until most of the vanadium has decayed. This can readily be seen by observing the count rate of the standard. The count time is then gradually increased to a maximum of 8 min and the decay of the ^{101}Tc followed for a few half lives. The relatively long total time needed for this, introduced an additional problem in that the vanadium cupferrate in chloroform is not stable for sufficiently long periods at the concentrations involved. This problem was solved by back-extracting with sodium hydroxide and addition of methanol to the final extract. This normally resulted in a sufficiently stable solution. Back-extraction with ammonia normally resulted in the appearance of a precipitate within one hour or less.

RESULTS

Rocks

The vanadium contents of the "standard" rocks G-1 and W-1 were obtained by neutron activation. The results, which have briefly been published before[12], are again presented in Table II. For comparison purposes the vanadium figures obtained by various other workers are also recorded. These figures agree fairly well with the general trend of those by most other workers.

TABLE II

ANALYTICAL RESULTS FOR G-1 AND W-1 (P.P.M.)

	Range of other workers[2,3,13,14]	*"Recommended" value*[13]	*90% confidence interval*[14]	*This work*	
				Individual determinations	*Average*
G-1	8–38	18	21 ± 7	13.4,13.2, 12.9,13.1, 13.0,13.0, 13.0,12.7	13
W-1	120–340	240	255 ± 55	250,244, 244,244, 247,244	246

A number of samples from various parts of the Skaergaard intrusion in East Greenland were kindly made available by Prof. L. R. WAGER of Oxford University and were also analysed. The results are given in Table III. Results for individual samples by other methods are not available, but these figures confirm the general shape of the vanadium distribution curve for this system, observed previously by spectrographic means[15]. It does seem, however, that the maximum vanadium concentration in a rock is higher than was realized before.

TABLE III

VANADIUM CONTENTS OF SAMPLES FROM THE SKAERGAARD INTRUSION OF EAST GREENLAND

Sample and origin	*Vanadium content, p.p.m.*
E.G. 4489, transgressive granophyre sill	0.8
E.G. 4332, hedenbergite granophyre	2.7
E.G. 4330, fayalite ferrogabbro	0.1
E.G. 4328, upper ferrogabbro	1.1
E.G. 5181, lower ferrogabbro	41
E.G. 4427, middle gabbro	1730
E.G. 1851, perpendicular feldspar rock	116
E.G. 4526, gabbro picrite	137
E.G. 4507, chilled marginal gabbro	190

Meteorites

The method was also applied to several available stony meteorites. The results, together with the latest abundance value for vanadium, as given by SUESS AND UREY[16], are recorded in Table IV. Again individual results for comparison are not available, but agreement between these results and the vanadium abundance for this type of material is fairly good.

TABLE IV

VANADIUM CONTENT OF METEORITES

Sample	*Individual results p.p.m.*	*Average p.p.m.*	*Abundance in p.p.m. in:*
Felix, Alabama	76.9, 75.0, 77.9	77	*Silicate Meteorites*
Hendersonville	62.5, 62.6, 60.6	62	73[a]
Eli-Elwah	65.0, 62.1	63	
Chateau-Renard	64.3, 65.7, 66.6	65	
Dhurmsala	64.7, 65.2, 67.3	66	
			Iron Meteorites
Canyon Diablo		<0.2	6[17]
Carlton		<0.2	5[18]

[a] Calculated from values given by SUESS AND UREY[16]

An attempt was also made to determine the vanadium content of two iron meteorites. In this case the sample was dissolved in hot dilute sulphuric acid to which a few drops of nitric acid were added, followed by addition of 5 mg vanadium carrier and sufficient potassium permanganate to produce a permanent pink colour. After a few minutes the solution was neutralized with 8 *N* sodium hydroxide and a few ml in excess added, followed by boiling for a few seconds. After centrifuging and decanting, the solution was treated and finally counted exactly as described for samples in presence of molybdenum interference.

The results are also shown in Table IV together with proposed abundances for this type of material. The present results must only be regarded as maximum values, as even detection of vanadium in these materials at this level becomes very difficult with the present method. These results do, however, indicate that the levels of vanadium to be expected in these materials, are much lower than the proposed values.

Nuclear interference

Possible errors which may arise by nuclear processes other than the (n, γ) reaction, must be considered. Of these (n, p), (n, α) and (γ, p) are the most likely. Apart from the (n, γ) reaction with ^{51}V, ^{52}V may be produced by any of the following nuclear reactions:

$$^{52}_{24}\mathrm{Cr} + {}^{1}_{0}n \rightarrow {}^{52}_{23}\mathrm{V} + {}^{1}_{1}\mathrm{H} \quad (n,p)$$

$$^{53}_{24}\mathrm{Cr} + \gamma \rightarrow {}^{52}_{23}\mathrm{V} + {}^{1}_{1}\mathrm{H} \quad (\gamma,p)$$

$$^{55}_{25}\mathrm{Mn} + {}^{1}_{0}n \rightarrow {}^{52}_{23}\mathrm{V} + {}^{4}_{2}\mathrm{He} \quad (n,\alpha)$$

The extent to which these reactions take place in the "rabbit" position, was determined as follows:

1. *The (n,p) and (γ,p) reaction on chromium.* 50 to 60 mg specpure chromium metal together with a suitable vanadium standard was irradiated in the normal way for 12 min. The metal was then dissolved by boiling with a few ml hydrochloric acid in a centrifuge tube. After removal of most of the hydrochloric acid by boiling with perchloric acid, 5 mg vanadium carrier and sufficient potassium permanganate to produce a pink colour were added to the hot solution. A few minutes were allowed for exchange, after which the vanadium was separated and purified by repeated extraction as already described, each extraction being performed in the presence of Cr^{+3} carrier solution. The final extract was filtered and counted in the normal way.

The average of two determinations gave 4.8 p.p.m. as the total vanadium obtained from the chromium metal. It is to be expected that at least part of the activity separated in this way, is due to vanadium impurity in the chromium. Nevertheless, the maximum error introduced as a result of the (n,p) and (γ,p) reactions on chromium will be not more than 0.05 p.p.m., as the general level of chromium in the samples analysed is well below 1%.

2. *The (n,α) reaction on manganese.* 40 to 50 mg specpure manganese oxide was irradiated for not more than 5 min and possible vanadium activity separated and purified exactly as described for rock samples. Because of the relatively high cross section of manganese for thermal neutrons, longer irradiations could not be made as the sample became too active for normal handling. As a result, the observed activity was very low. However, the total vanadium separated from manganese oxide was less than 0.5 p.p.m. Thus, even in the presence of as much as 10% manganese oxide, the maximum error introduced by the (n,α) reaction on manganese, is of the order of 0.05 p.p.m.

ACKNOWLEDGEMENT

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SUMMARY

A method for the determination of vanadium by neutron activation analysis and its application to a variety of materials is outlined. The vanadium is separated from the irradiated material by chloroform–cupferron extractions, and the activity determined by liquid counting. The only interfering elements are molybdenum and technetium and then only in samples with relatively low vanadium content. The extent of conflicting nuclear reactions was investigated.

RÉSUMÉ

Les auteurs proposent une méthode de dosage du vanadium par activation au moyen de neutrons. Le vanadium est ensuite séparé de l'échantillon irradié par des extractions chloroforme–cupferron.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Vanadium durch Aktivierung mit Neutronen; die Abtrennung des Vanadiums erfolgt durch Extraktion mit einer Cupferron–Chloroform Lösung.

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THE DETERMINATION OF SCANDIUM IN ROCKS AND METEORITES BY NEUTRON-ACTIVATION ANALYSIS*

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INTRODUCTION

Scandium is one of the rare but widely distributed elements and its chemistry did not attract much attention during the past years, mainly because of lack of important industrial applications. However, from a geochemical point of view it is an important element, more so because it lies on the minimum of the abundance curve of the elements.

Most of the results for the determination of scandium in geochemical material have been obtained by spectrographic methods, the sensitivity of which is about 2 p.p.m.[2]. Recently[3] scandium has been determined in a number of iron meteorites by neutron activation analysis. In this case most of the scandium was formed as a result of cosmic ray bombardment on the meteorite in space. The results obtained were of the order of 10^{-3} p.p.m. which demonstrates the high sensitivity to be obtained for this particular element. More recently[4], after the present work has been concluded, the method of neutron activation analysis was applied to the determination of scandium in chondrites.

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* This paper was originally reproduced as a U.K.A.E.A. Report[1]. It is presented here in a slightly modified form.

It has been calculated[5] that the sensitivity for determining scandium by neutron activation in a neutron flux of 10^{12} neutrons per square cm per second is $5 \cdot 10^{-11}$ g. This would make the method of neutron activation admirably suitable for checking the existing spectrographic results and for obtaining results beyond the sensitivity of the latter method.

Feasibility of the neutron-activation method

The high theoretical sensitivity for scandium mentioned above is the *result of 100% isotopic* abundance of ^{45}Sc coupled with a relatively high activation cross (23 barns) for thermal neutrons to form ^{46}Sc. This would, at a first glance, make scandium a very favourable element to determine by neutron activation. There are, however, a number of complications which must first be considered.

^{46}Sc and a series of other radioactive scandium isotopes are formed by the action of fast neutrons on titanium by the (*n,p*) reaction. Although the cross sections involved are of the order of a few millibarns or less[6], the error introduced could be serious because of the relatively high titanium content of some geochemical samples. The (*n,p*) reaction on titanium has been used to prepare ^{46}Sc for half life determinations[7] which is added proof that the reaction cannot be neglected.

If the activity is finally determined by total β- or γ-counting, this error will not only be due to spurious ^{46}Sc formed by the above reaction. Indeed the error will be greatly increased by the added activity of the other scandium isotopes. Two of these isotopes are also produced by the (*n*,α) reaction on vanadium. In calcium rich samples the error will be still further increased because of formation of radioactive scandium

TABLE I

NUCLEAR DATA FOR THE FORMATION OF Sc-ISOTOPES

Target Nuclide	*Abundance of nuclide in natural element, %*	*Isotopic activation cross section*	*Product of irradiation*	*Radiation and energy of product nuclide*	*Half life*	*Nuclear reaction involved*
^{45}Sc	100	23 b	^{46}Sc	β^- 0.36 γ 0.89	85 d	(*n*,γ)
^{46}Ti	8	4·1 mb	^{46}Sc	1.12		(*n,p*)
^{47}Ti	7·4	0.21 mb	^{47}Sc	β^- 0.44 0.60	3·4 d	(*n,p*)
^{50}V	0.25		^{47}Sc	γ 0.16		(*n*,α)
^{46}Ca	0.0032	0.3 b	^{47}Sc			(*n*,γ) followed by β-decay
^{48}Ti	73·8	0.077 mb	^{48}Sc	β^- 0.64 γ 1.32	44 h	(*n,p*)
^{51}V	99·75		^{48}Sc	1.04 0.99		(*n*,α)
^{49}Ti	5·5		^{49}Sc	β^- 2.0 no γ	57 min	(*n,p*)
^{48}Ca	0.18	1.1 b	^{49}Sc			(*n*,γ) followed by β-decay
^{50}Ti	5·3		^{50}Sc	β^- 3.5 γ 1.6 1.2	1.7 min	(*n,p*)

isotopes by β-decay of ^{47}Ca and ^{49}Ca which in turn are produced by the action of thermal neutrons on natural calcium.

Table I summarises the data for all the nuclides involved in the above discussion. It is quite clear from this table that interference from ^{49}Sc and ^{50}Sc will not be of a serious nature as both will have decayed away completely within half a day. It is thus only necessary to consider interference from ^{47}Sc and ^{48}Sc.

Both these scandium isotopes are β-emitters with β-energies fairly close together and also fairly close to that of ^{46}Sc. Discrimination between the three isotopes by β-counting would thus not be very easy.

Both are also γ-emitters with γ-energies relatively widely separated. However, the γ-spectrum of ^{48}Sc overlaps that of ^{46}Sc. This difficulty is, however, not serious as the difference in half lives of ^{46}Sc and ^{48}Sc is so large that the ^{48}Sc can be allowed to decay away completely without any serious reduction in the activity of ^{46}Sc. After decay of ^{48}Sc, it should be easy to distinguish between ^{46}Sc and ^{47}Sc on the γ-spectrometer.

It is of course not possible to distinguish between ^{46}Sc formed by the (n,γ) reaction on ^{45}Sc and ^{46}Sc formed by the (n,p) reaction on ^{46}Ti. The extent of this interference had to be determined experimentally for the irradiation position used.

The magnitude of the ^{46}Ti (n,p) ^{46}Sc reaction

Suitable quantities (130 to 140 mg) of "Specpure" titanium metal sponge were weighed into small dry silica ampoules of 4 to 6 mm internal diameter and immediately sealed. Weighed quantities (50–100 mg) of a suitable scandium standard were treated similarly. Samples and standards were packed side by side in a standard irradiation can and irradiated in the "self-serve" position of the Harwell Pile, BEPO, for 36 h.

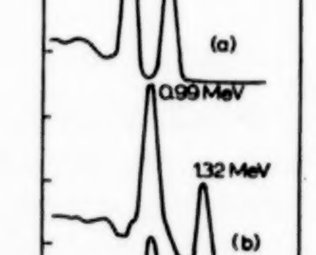

Fig. 1. γ-Spectra of ^{46}Sc and ^{47}Sc.
(a) ^{46}Sc-standard. (b) – (e) Sc from Ti. (b) 24 h after end of irradiation. (c) Approx. 5 d after end of irradiation. (d) Approx. 11.5 d after end of irradiation. (e) Approx. 19 d after end of irradiation.

After irradiation the samples were left overnight for shortlived activities to decay away.

After addition of appropriate quantities of scandium carrier solution, ^{46}Sc was separated from the titanium and purified as described below. Treatment of the standards is also described below.

The samples separated from the irradiated titanium were examined on a hundred-channel γ-spectrometer with intervals over a period of a few weeks. The results are shown in Fig. 1. From this series of spectra it is clear that 24 h after the end of irradiation (b) the only peaks clearly distinguishable are those of ^{48}Sc with almost no sign of the ^{46}Sc peaks. After about five days (c) the ^{46}Sc peaks become more visible and after about 11.5 days (d) the ^{48}Sc are only just visible. Finally after about 19 days the only peaks distinguishable are those of ^{46}Sc. At this point the total scandium from titanium was calculated and values of 1.57 and 1.62 p.p.m. found for two samples.

The possibility now existed that part or all of this ^{46}Sc was due to scandium impurity in the titanium. To determine this, samples and standards were again prepared as before but irradiated this time for four weeks in a thermal hole in the pile at a neutron flux of approximately $3 \cdot 10^9$ neutrons per square cm per second. Under these conditions the fast neutron flux would be so low that any ^{46}Sc found could be assumed as almost entirely due to scandium impurity in the titanium.

After separation of the scandium as before, the samples were examined on the γ-spectrometer. No sign of any ^{46}Sc could be observed after a 100-min count. This means that the maximum error that would be introduced by the (n,p) reaction on titanium, is of the order of 1.6 p.p.m. for the irradiation position used. The error introduced in this way would only be significant in samples with relatively high titanium content (say $> 5\%$) and relatively low scandium content (say < 0.1 p.p.m.). In these cases the difficulty can be overcome by irradiation in a thermal hole or alternatively a correction for the contribution in titanium could be made if the titanium content of the samples are accurately known.

EXPERIMENTAL

Irradiation

The samples were already ground to 100 or 200 mesh. Suitable triplicate quantities of sample (30 to 150 mg) were sealed in silica ampoules. Weighed duplicate quantities (50 to 100 mg) of dilute aqueous standard solutions of scandium chloride in dilute hydrochloric acid were likewise sealed in similar silica ampoules. Samples and standards were packed side by side into standard 3-inch × 1-inch aluminium cans and irradiated in the "self-serve" position of the Harwell Pile, BEPO, for from 12 to 36 h (flux about $10^{12} n/\text{cm}^2/\text{sec}$).

Chemical separation

Recently WÄNKE[3] described a procedure for the separation and purification of scandium from irradiated iron meteorite samples. This procedure is elaborate because of the very low scandium content of the samples, the final precipitate being scandium oxide.

Other procedures describe the separation of scandium from cyclotron bombarded copper[8] and the determination of radio-scandium in presence of fission product material[9].

These procedures are all too elaborate or not suited to the particular materials to be analysed. It was thought desirable to devise a somewhat simplified purification procedure, preferably one which allows for the use of only a few mg of scandium carrier initially. The reason for this is that scandium compounds are relatively expensive and only "Specpure" compounds were available at the time. This means that, if chemical yield was to be determined gravimetrically on an ordinary chemical balance, a suitable gravimetric reagent for scandium had to be found. The properties of this compound should be so as to precipitate 2–3 mg of scandium fairly quantitatively, be fairly insoluble in water and give a final source suitable for γ-counting.

Most of the known scandium compounds do not possess these properties and after a large number of attempts with different compounds it was decided to use the one with benzene–sulphinic acid. This compound precipitates from acid solution by the addition of a sodium–benzene–sulphinate solution to a scandium solution and appears to be very insoluble in water. Preliminary experiments indicated that this pure white compound may be suitable for the gravimetric determination of scandium.

The separation procedure finally adopted consists of dissolution of the sample by sodium peroxide fusion followed by two stages of solvent extraction. 5–6 mg of inactive scandium were added as carrier initially and the radiochemically pure element obtained from the chemical separation was precipitated and mounted for counting as the benzene–sulphinate. The chemical yield was determined gravimetrically on this compound; it was usually about 60 to 70%.

Measurement of radioactivity

The final precipitate was counted on a 3-inch × 3-inch sodium iodide thallium activated scintillation crystal associated with a suitable amplifier and a hundred channel "kick-sorter". The attenuation of the amplifier was always adjusted so as to observe any gamma energy from about 0.4 to about 3.5 MeV on the "kick-sorter". For calculation purposes the total area under both peaks of ^{46}Sc (see Fig. 1a) was used after suitable corrections for background and paralysis losses had been made.

REAGENTS

Scandium carrier solution

Weigh out as rapidly as possible about 1.68 g anhydrous scandium chloride, dissolve in water and sufficient hydrochloric acid to give a clear solution and dilute to 500 ml in a volumetric flask. 1 ml $\equiv$ *ca*. 1 mg Sc.

Dilute standard scandium solution

Dilute a known volume of the above carrier solution with water and a few drops of hydrochloric acid in a suitable volumetric flask to give a final concentration of approximately 20 μg of scandium per ml. Determine the density of the solution by weighing 10.0 ml.

Determine the exact concentration of the carrier solution gravimetrically as scandium oxinate by the method of POKRAS *et al.*[10]. From this the exact concentration of the standard solution can be calculated.

Hydrochloric acid, sp.gr. 1.18; perchloric acid, 72 %; nitric acid, sp.gr. 1.42; ammonia solution, *ca.* 10 *N*; cupferron solution, 6% in water; ammonium thiocyanate, 500 g/l; sodium benzene sulphinate, 4% solution in water; chloroform, Laboratory reagent; ether, di-ethyl ether; sodium peroxide, powdered.

PROCEDURE

Procedure for rocks and meteorites

Prepare irradiation ampoules about 6.5 cm long from silica tubing having an internal diameter of about 4 mm, each with a constriction near the open end. Weigh out accurately an appropriate quantity of the finely ground sample into each ampoule and seal off. Likewise seal off known amounts of the dilute standard scandium solution into similar ampoules. Pack the standards and samples side by side in a standard irradiation can and irradiate for 12 to 36 h, depending on the scandium content. After allowing sufficient time for the can to "cool" behind a radiation shield, the samples can be separated and purified at any convenient time during the next fourteen days. No counting for calculation purposes was ever made within fourteen days after the end of irradiation. The reasons for this have already been discussed.

Remove the ampoules from the can, open them at the constriction, and transfer the solid samples to 5-ml nickel crucibles containing about 2 g powdered sodium peroxide, mix thoroughly and cover the mixture with a thin layer of sodium peroxide. Carefully fuse the mixture by holding the crucible in the flame of a bunsen burner with a metal tong, and then heat to a dull red heat. Then quickly cool the crucible by immersing the bottom half in cold water. Put the crucible on its side in a 250-ml tall form beaker containing 5.0-ml scandium carrier solution at a total volume of about 12 ml and cover immediately with a watch glass. As soon as the initial vigorous reaction subsides, neutralise the solution with hydrochloric acid to obtain a clear solution and add a few drops in excess. Determine by visual inspection if dissolution of the sample is complete. This was always found to be the case.

After a few minutes transfer the green solution to a 50-ml centrifuge tube and precipitate the scandium (and other cations) by addition of excess ammonia. Centrifuge, decant, dissolve the precipitate in dilute hydrochloric acid and repeat the precipitation etc. once more.

Dissolve the precipitate in about 2 ml hydrochloric acid, dilute to about 20 ml with water and transfer to a 100-ml separating funnel. Add 5 or more ml of cupferron solution and extract with about 20 ml chloroform. Leave to settle, separate and discard the organic layer. Repeat once or twice more and finally extract with about 20 ml chloroform alone. In these extractions cations like iron, titanium etc. are separated from the scandium as the latter is practically not extracted under these conditions.

Transfer the aqueous phase to a 250-ml beaker, add nitric acid and destroy organic matter by boiling on a hot plate (add more nitric acid if necessary). Finally add a few ml of perchloric acid and take to fumes. Leave to cool, dilute to 10 to 15 ml, heat and filter off any silica. Run the filtrate into a 50-ml centrifuge tube, precipitate the scandium by addition of excess ammonia, centrifuge, decant and discard the supernate. Dissolve the precipitate in about 4 ml hydrochloric acid, dilute to about 20 ml and transfer the solution to a 250-ml separating funnel. Add 50 ml ammonium thiocyanate solution and extract the scandium thiocyanate complex twice with 50 ml ether each time. Transfer the combined ether phases to a 250-ml beaker, add about 10 ml water and leave in a good fume hood to evaporate off the ether.

Heat the aqueous solution on a hot plate and destroy the thiocyanate by cautious, drop-wise addition of nitric acid. When the vigorous stage of the reaction has passed, add 5 to 10 ml more nitric acid and boil to obtain a clear solution. Then add a few ml of perchloric acid, more nitric acid and take to strong fumes. Remove from hot plate, leave to cool, and take up the residue in about 10 ml water and filter if necessary. Transfer the solution to a centrifuge tube, precipitate the scandium by addition of excess ammonia, centrifuge, decant and discard the supernate.

Dissolve the precipitate in the minimum quantity of hydrochloric acid, dilute to about 5 ml with water and add sufficient ammonia to produce a permanent precipitate. Add two drops 3 N hydrochloric acid to obtain a clear solution and precipitate the scandium by addition of 4 ml sodium–benzene–sulphinate solution. Centrifuge and decant the supernate. Wash the precipitate three times with about 5 ml water each time. Make a slurry of the precipitate with a small amount of water and transfer with a drop-pipette to a tared aluminium counting tray. Dry slowly under an infra-red lamp, cool, and weigh to determine the chemical yield.

It may, of course, sometimes be necessary to repeat one or both of the extraction stages with addition of suitable holdback carriers. However, this was never found to be necessary in the samples analysed.

Standards

When time permits, open the ampoules containing the scandium standards. Transfer the solution quantitatively to a suitable volumetric flask by means of dilute hydrochloric acid and a drop-pipette drawn out to a capillary. After dilution to the mark and mixing, a suitable aliquot is measured out into a centrifuge tube containing 5.0-ml scandium carrier solution. Mix thoroughly and precipitate the scandium by addition of excess ammonia followed by centrifugation and decantation of the supernate.

Dissolve the precipitate in 4 ml hydrochloric acid, dilute to about 20 ml and transfer to a 250-ml separating funnel. Add 50 ml ammonium thiocyanate and extract the scandium thiocyanate complex once with 50 ml ether. After separation of the phases, the ether phase is treated exactly as described for the samples above.

Procedure for titanium

Transfer the irradiated titanium to a 250-ml beaker containing 5.0 ml scandium carrier solution and a few ml of perchloric acid. Heat on the hot plate and add dilute hydrofluoric acid little by little until all the titanium is dissolved. Then take to strong fumes of perchloric acid. Leave to cool, add a few ml of water and again take to fumes. After cooling add about 10 ml water, heat, centrifuge in a 50-ml tube and decant the supernate into a clean tube. Precipitate the scandium (and titanium) by addition of excess ammonia, centrifuge, decant, dissolve the precipitate in 1 to 2 ml hydrochloric acid and dilute to about 20 ml. Remove any titanium by repeated extraction with cupferron and chloroform and treat the resulting aqueous solution exactly as described for samples above.

Counting

The paralysis time of the gamma spectrometer was relatively high (780 μsec). In order to keep the correction factor below about 10%, samples had normally to be counted at low geometry and sufficiently long counting times to obtain good statistical accuracy.

As the half life of the isotope involved is too long to make half life determinations practical, agreement between the gamma spectra of samples and standard with respect to gamma energies and relative peak heights was considered to be sufficient proof to confirm radiochemical purity.

TABLE II

SCANDIUM RESULTS FOR G-1 AND W-1 IN p.p.m.

	Other workers[a]	*Ahrens recommended value*[a]	*This work Individual results*	*Average*
G-1	n.d., 2, 4, –, <3, –	3	2.72, 2.86, 2.76 2.77, 2.84	2.8
W-1	15, 34, 51, 50, 35, 36.	37	34·1, 34·8 33·5, 33·5	34

[a] Taken from AHRENS[11].

RESULTS

Rocks

The results of analysis of the "standard" rocks W-1 and G-1 are given in Table II together with results by other workers. These results have briefly been published before[12]. Results of the present work seem to agree with the general trend of those by other workers. Agreement with the "recommended" valve by AHRENS[11] is also very good in both cases, but this is fortuitous as the latter value is merely a mean value of all previous results.

TABLE III

SCANDIUM CONTENT OF ROCKS FROM THE SKAERGAARD INTRUSION

Sample and origin		*Sc-content, p.p.m.*	*Average, p.p.m.*
E.G. 4489	Transgressive Granophyre sill	7·48, 7·37, 7·71	7·5
E.G. 4332	Hedenbergite Granophyre	21·4, 20.9, 22.2	21.5
E.G. 4330	Fayalite Ferrogabbro	39·5, 40.0, 40.3	40
E.G. 5181	Hortonolite Ferrogabbro	33, 35·4, 35, 33·4	34
E.G. 4427	Middle Gabbro	49·7, 53·4, 52·4	52
E.G. 1851	Perpendicular Feldspar rock	20.3, 19.1, 19.9	20
E.G. 4526	Gabbro Picrite	19.9, 19.9, 19.8	20
E.G. 4507	Chilled marginal Gabbro	26.6, 25.8, 27.2, 25.6	26

A number of samples from various parts of the Skaergaard intrusion of East Greenland, kindly provided by Prof. L. R. WAGER, were also analysed. The results are given in Table III. These results also agree fairly well with the general trend observed previously by spectrographic means[13].

Meteorites

No iron meteorites were analysed as this has already been done by WÄNKE[3] who showed that most of the scandium was of cosmic origin. Several stony meteorites were, however, analysed. The results, together with the latest abundance value for scandium in stony meteorites, are shown in Table IV. Individual results for these samples by other methods are not available, but agreement between these values and the abundance value for this type of sample is very good. The very recently reported results by BATE *et al.*[4] are in excellent agreement with those reported here.

TABLE IV

SCANDIUM CONTENT OF SOME STONY METEORITES

Meteorite	*Scandium content, p.p.m.*	*Average, p.p.m.*	*Abundance, p.p.m.,*[a] *in stony meteorites*
Hendersonville	7.89, 8.0, 8.1, 7.65	7.9	8.3
Dhurmsala	8.22, 8.15, 8.0	8.1	
Eli-Elwah	8.05, 8.65, 8.5	8.4	
Chateau-Renard	8.5, 9.0, 9.13, 8.74	8.8	
Felix, Alabama	9.69, 9.53, 9.96	9.7	

[a] Calculated from abundance value given by SUESS AND UREY[14].

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SUMMARY

A method for the determination of scandium in geochemical material by neutron activation analysis is outlined. A relatively simple radiochemical separation from the components of the irradiated sample was employed to provide a final source for gamma spectrometry. Sufficient "cooling" time has to be allowed to prevent interference by a short lived scandium isotope. After investigation of the magnitude of the (*n,p*) reaction on titanium, various rock and meteorite samples were analysed, including the "standard" rocks, G-1 and W-1.

RÉSUMÉ

Une méthode est proposée pour le dosage du scandium par activation au moyen de neutrons. Une séparation radiochimique relativement simple d'avec les constituants de l'échantillon irradié a pu être effectuée. Divers échantillons de roches et de météorites ont été analysés.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Scandium durch Aktivierung mit Neutronen und radiochemische Trennung von den anderen Komponenten. Analysenergebnisse einer Anzahl Gesteinen und Meteoriten werden mitgeteilt.

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STUDIES OF THE SOLVENT EXTRACTION OF SILVER OXINATE

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INTRODUCTION

Oxinate extractions

Oxine has long been recognized and used as a reagent for the analytical determination of numerous metal ions[1]. Some work has been carried out on the solvent extraction of metal ions from aqueous solutions into organic phases containing oxine, but few detailed theoretical studies have been made. Among the better of the latter type is the study of the extraction of the oxinates of aluminum, gallium, and indium by LACROIX[2]. He established curves showing the partition of metal ion between chloroform and water as a function of pH and provided quite adequate theoretical treatment.

Extraction equations

Numerous authors[3-5] have employed the following equation to describe simple solvent extraction systems as described above

$$E = \frac{K(HR)_o^n}{(H)^n} \qquad (1)$$

where E designates the ratio of metal concentration in the non-aqueous phase to the metal concentration in the aqueous phase, K is the extraction constant which is made up of several other more fundamental constants, $(HR)_o$ signifies the concentration of the oxine in the organic phase, (H) designates the concentration of the hydrogen ion in the aqueous phase, and n signifies the valence of the metal ion. By taking the logarithm of equation (1), the following relation which holds at 50% extraction is obtained

$$n\mathrm{pH}_{1/2} = -\log K - n \log(HR)_o \qquad (2)$$

where $\mathrm{pH}_{1/2}$ symbolizes the pH value at which 50% extraction occurs.

The effect on extractions of species in the aqueous phase which react with the metal ion to form soluble complexes has also received both theoretical and experimental treatment[3-6]. These treatments provide the following modification of equation (1)

$$E' = \frac{K(HR)_o^n}{F(H)^n} \qquad (3)$$

in which E' is the extraction ratio under the complexing conditions and F is defined as follows

$$F = \Sigma K_i(X)^i, \text{ with } K_0 = 1 \tag{4}$$

where the K values represent the successive stability constants of the soluble complexes and (X) represents the concentration of the free complexing agent X. If the logarithm of equation (3) is taken, the following relation holds at 50% extraction

$$n\text{pH}_{1/2} = -\log K - n \log (HR)_o + \log F \tag{5}$$

Equation (5) is of considerable import, since if n, $(HR)_o$, and F are known for an extraction, one may with a knowledge of the value of either one of the terms K or $\text{pH}_{1/2}$ calculate the other. The possibility for the determination of stability constants of the aqueous complexes also presents itself.

Present problem

In the present work a study was made of the extraction of silver oxinate from aqueous solutions into organic media containing oxine as the pH of the aqueous solutions was varied. The effects of oxine concentration, non-aqueous medium, temperature, and the presence of water-soluble complexing agents on the extraction were investigated.

EXPERIMENTAL

The chemicals, apparatus, and procedures used in this investigation were essentially those as described in our previous work[4]. The oxine was purified by recrystallization from ligroin[7]. 10-ml portions of the aqueous phase were stirred with 10-ml portions of the organic phase containing the oxine for 5 h. The silver ion in the aqueous phases was approximately 10^{-7} M and was radioactively labelled to facilitate measurements of the extraction.

RESULTS

The experimental results are presented in Table I. In all cases, the curves of per cent silver extracted into the organic phase plotted against pH exhibited the typical S-shaped pattern shown by systems of this type[3]. The pH values at which 50% of the silver had been extracted, $\text{pH}_{1/2}$, are indicated in the table. It was observed that all extraction curves tended to drop off to 0% extraction just above a pH of 9.0.

INTERPRETATION

The slopes of all extraction curves near the $\text{pH}_{1/2}$ showed values of 55 ± 10 agreeing with the predicted slope of 57 for a 1 : 1 silver–oxine complex. Using the data of Systems 1–3 and 23–29, an n value of 1, and equation (2), values of log K were calculated. These are recorded in the last column of Table I.

Equation (2) predicts that a change in the oxine concentration by a factor of 10 should produce a change in $\text{pH}_{1/2}$ of 1.0 unit. This does not seem to be the case in Systems 1–3, although an increase in oxine concentration does shift the $\text{pH}_{1/2}$ to a lower value as predicted. The deviations might be explained by studies of the activities of the various involved entities.

Water-soluble complexing agents caused shifts in the $\text{pH}_{1/2}$ value as can be seen from an examination of Systems 2 and 6–22. Using equation (5), the value of log K from System 2, and stability constants from the literature[8] to obtain F, predicted

TABLE I

RESULTS OF EXTRACTION EXPERIMENTS

System	*Organic Phase*	*Oxine Concn. (M)*	*Aqueous Phase*[a]	*Temp. (°C)*	*Obs. $pH_{1/2}$*	*Calc. Values*
1	$CHCl_3$	10^0	10^{-1} *M* $NaClO_4$	30	3.0	log *K* = -3.0
2		10^{-1}			6.9	-5.9
3		10^{-2}			8.8	-6.7
4		10^{-4}			[b]	
5		10^{-5}			[b]	
6		10^{-1}	10^{-1} *M* KNO_3		6.9	pH$_{1/2}$ = 6.9[d]
7			10^{-1} *M* $NaC_2H_3O_2$		7.0	7.1[d]
8			10^{-1} *M* NaC_2O_4		7.1	6.9[d]
9			10^{-1} *M* $Na_3C_6H_5O_7$[c]		7.5	
10			10^{-1} *M* KCl		[b]	pH$_{1/2}$ = 10.3[d]
11			10^{-2}		8.2	8.5[d]
12			10^{-3}		7.5	7.4[d]
13			10^{-1} *M* KBr		[b]	13.0[d]
14			10^{-2}		[b]	11.7[d]
15			10^{-3}		[g]	9.4[d]
16			10^{-1} *M* KI		[b]	17.9[d]
17			10^{-2}		[b]	16.1[d]
18			10^{-3}		[b]	11.9[d]
19			10^{-1} *M* $Na_2S_2O_3$		[b]	18.5[d]
20			10^{-2}		[b]	16.4[d]
21			10^{-3}		[b]	14.7[d]
22			10^{-1} *M* glycine		7.1	10.4[d]
23			10^{-1} *M* $NaClO_4$	0	5.8	log *K* = -4.8
24				40	7.8	-6.7
25	CCl_4			30	7.2	-6.2
26	C_6H_6				6.8	-5.8
27	$C_6H_5CH_3$				7.4	-6.4
28	C_6H_5Cl				6.6	-5.6
29	C_6H_5Br				6.5	-5.5
30	$C_4H_9OC_4H_9$[e]				[b]	
31	C_6H_{12}[f]				[b]	

[a] In all cases the silver concentration in the original aqueous phase was approximately 10^{-7} *M*, and all solutions were made up to an ionic strength of 0.10 with $NaClO_4$ if necessary.
[b] No extraction in the pH range of 2–10.
[c] Sodium citrate.
[d] See reference 8 for stability constants.
[e] *n*-Butyl ether.
[f] Cyclohexane.
[g] About 20% extraction at pH of 9.5.

pH$_{1/2}$ values for a number of these systems were calculated. These are recorded in the last column of Table I. Judging from the fact that the authors had to select stability constants in some cases from many sets of conflicting data and from the knowledge that the pH$_{1/2}$ values are probably good to ± 0.2 pH units, the agreement is quite acceptable. At a pH of about 9.5, about 20% extraction was observed for the 10^{-3} *M* KBr solution.

The drop off to 0% extraction which occurred with all extraction curves just beyond a pH of 9.0 can be explained in terms of the data of LACROIX[2] and MOELLER AND

PUNDSACK[9]. Their investigations give the distribution ratio of oxine in chloroform to oxine in water as a function of the pH of the aqueous phase. The distribution ratio is small at pH values below 3.5 and above 9.5, thus indicating that extraction at pH values outside these limits will not be too effective because of the decreased amount of oxine in the organic phase.

A straight line relation between log K and the reciprocal of the absolute temperature was observed for the data of Systems 2, 23, and 24. The slope of the line was found to be $4 \cdot 10^3$ Å, which gives an equation of this form: $\log K = (4 \cdot 10^3)T^{-1} - 19.3$. The enthalpy of the extraction reaction which is equal to $-2.3\ R$ (slope) calculates out to be about —18 kcal/mole, and the free energy values as obtained from $2.3\ RT \log K$ are about —6, —8, and —10 kcal/mole at 0°, 30° and 40°. Entropy calculations give an average value of about —3 e.u. over the temperature range studied.

SUMMARY

A study of the extraction of 10^{-7} M silver ion from various aqueous solutions into various organic solvents containing oxine has been carried out. The effects of pH, the presence of water-soluble complexing agents, oxine concentration, and temperature have been investigated. Extraction constants have been calculated and theoretical interpretations of the data are offered.

RÉSUMÉ

Une étude a été effectuée sur l'extraction de l'oxinate d'argent par divers solvants organiques. Les constantes d'extraction ont été calculées.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Extraktion von Silberoxinat aus verschiedenen wässrigen Lösungen mit verschiedenen organischen Lösungsmittel und Angabe der Extraktionskonstanten.

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THE THERMAL DECOMPOSITION OF THE URANYL AND SODIUM URANYL CARBONATES

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INTRODUCTION

The ability of uranium to form soluble compounds in sodium carbonate and bicarbonate solutions is the basis of an important extractive technique. In addition to the binary carbonate[1] UO_2CO_3, four sodium uranyl carbonates have been reported[2]. These are: Sodium uranyl dicarbonate, $Na_2UO_2(CO_3)_2$; Sodium uranyl tricarbonate, $Na_4UO_2(CO_3)_3$; Sodium diuranyl pentacarbonate, $Na_6(UO_2)_2(CO_3)_5$; Sodium trioxyuranic diuranyl pentacarbonate, $Na_6(UO_2)_2(UO_3)_3(CO_3)_5$.

The most important of these is the tricarbonate. This form, in which uranium is combined with the largest proportion of carbonate, occurs as the ion $UO_2(CO_3)_3^{-4}$ in ore leach liquors containing excess sodium carbonate. The various preparative methods described by Bachelet *et al.* and Blake *et al.* were followed. Table I indicates the reactions found most useful. As in earlier preparations, the sodium uranyl carbonates were not obtained as definitely stoichiometric compounds.

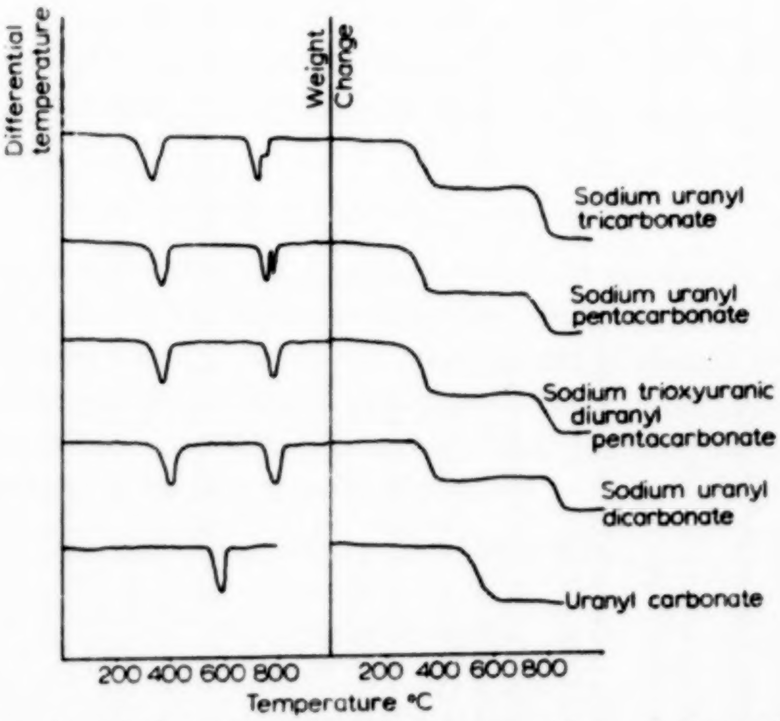

Fig. 1. Differential thermal and thermogravimetric decomposition of the sodium uranyl carbonates and uranyl carbonate.

TABLE I

PREPARATION AND COMPOSITION OF THE SODIUM URANYL CARBONATES

Compound	Method of Preparation	Composition					
		Sodium (Na,%)		Uranium (U,%)		Carbon (C,%)	
		Calc.	Found	Calc.	Found	Calc.	Found
Uranyl carbonate UO_2CO_3	$UO_3 + CO_2 = UO_2CO_3$ (under pressure)	—	—	72.1	71.9	3.64	3.70
Sodium uranyl tricarbonate $Na_4UO_2(CO_3)_3$	$UO_3 + 4NaHCO_3$ $= Na_4UO_2(CO_3)_3 + 2H_2O + CO_2$	17.3	16.5	43.7	43.1	6.63	6.44
Sodium diuranyl pentacarbonate $Na_6(UO_2)_2(CO_3)_5$	$2UO_3 + 6NaHCO_3$ $= Na_6(UO_2)_2(CO_3)_5 + 3H_2O + CO_2$	13.8	14.6	48.9	52.6	6.15	5.80
Sodium trioxyuranic diuranyl pentacarbonate $Na_6(UO_3)_3(UO_2)_2(CO_3)_5$	$3UO_3 + Na_6(UO_2)_2(CO_3)_5$ $= Na_6(UO_3)_3(UO_2)_2(CO_3)_5$	7.37	7.40	64.9	63.4	3.28	3.02
Sodium uranyl dicarbonate $Na_2UO_2(CO_3)_2$	$2NaHCO_3 + UO_3$ $= Na_2UO_2(CO_3)_2 + H_2O$	10.6	11.3	54.6	54.6	5.51	4.80

TABLE II

THERMOGRAVIMETRIC AND DTA DATA ON THE THERMAL DECOMPOSITION OF THE URANYL AND SODIUM URANYL CARBONATES

Compound	Technique					
	DTA		Thermogravimetry			
	First Peak °C	Second Peak °C	Weight Loss, 1st Stage,%		Weight Loss, 2nd Stage,%	
			Observed	Calculated	Observed	Calculated
$Na_4UO_2(CO_3)_3$ (SUTC)	430	840	12.5	12.15	3.6	4.00
$Na_6(UO_2)_2(CO_3)_5$	420	810, 840	15.0	13.5	4.5	4.50
$Na_6(UO_2)_2(UO_3)_3(CO_3)_5$	425	830	11.0	9.60	2.10	2.40
$Na_2UO_2(CO_3)_2$	440	850	17.0	15.15	4.50	5.01
UO_2CO_3	600	—	13.3	13.3	—	—

EXPERIMENTAL

Apparatus

Thermobalance: Stanton, mg-recording. Rate of heating, 5° per minute. Sample weight, 1 g.

Differential Thermal Analysis Equipment: horizontal furnace, longitudinally divided, supplied with a voltage increasing from 40 to 115 V through a gear-driven variable transformer. Inner ceramic tube, longitudinally halved, with Inconel sample block. Platinum, Platinum–10% Rhodium thermocouples. X–Y recorder with pre-amplifier. Rate of heating, 10° per min.

Thermal decomposition

Fig. 1 shows the results obtained by the thermogravimetric and differential thermal study of the reactions occurring when each compound was heated in air. The sodium uranyl carbonates show endothermic DTA peaks at moderate and at fairly high temperatures, each main peak being associated with a thermogravimetric weight loss. Uranyl carbonate differs in having only one decomposition stage. Obviously, there is a general similarity between the modes of decomposition of the sodium uranyl carbonates, which is not shared by the binary uranyl carbonate.

The quantitative results of this study are recorded in Table II. The calculated thermogravimetric weight losses result from formulae derived in a later section.

Thermal decomposition of uranyl carbonate

The observed weight loss is in accordance with the reaction:

$$UO_2CO_3 = UO_3 + CO_2 \qquad (1)$$

A molecular formula determination proved that the residue was UO_3.

Thermal decomposition of sodium uranyl tricarbonate

Two endothermic peaks, each with an accompanying weight loss, require explanation. All possible decomposition reactions will be considered in turn. The reaction:

$$Na_4UO_2(CO_3)_3 = Na_2UO_4 + Na_2CO_3 + 2CO_2 \qquad (2)$$

can be discarded on the grounds that no subsequent reaction between the products is possible, although the weight loss involved equals the sum of the thermogravimetric losses. (It will be seen later that the overall reaction can be expressed in this form). A simple dissociation:

$$Na_4UO_2(CO_3)_3 = UO_2CO_3 + 2Na_2CO_3 \qquad (3)$$

might, by itself, account for the first DTA peak, but not for the weight change involved. If followed immediately by reaction between the products, however, the observations would be accounted for; the first DTA peak would probably be compound if the reactions were not almost coincidental. A separate DTA experiment with mixed uranyl carbonate and sodium carbonate shows a broad endothermic peak at about 350°, indicating a reaction. A further possibility,

$$Na_4UO_2(CO_3)_3 = UO_3 + 2Na_2CO_3 + CO_2 \qquad (4)$$

followed by:

$$UO_3 + Na_2CO_3 = Na_2UO_4 + CO_2 \qquad (5)$$

or alternatively,

$$2UO_3 + Na_2CO_3 = Na_2U_2O_7 + CO_2 \qquad (6)$$

is unsatisfactory, primarily because the observed weight changes would not be accounted for. In addition, the necessary breaking of the uranium–carbonate bond has been shown, in the case of uranyl carbonate already considered, to require a temperature above that at which the first reaction occurs.

The only remaining possible reactions are:

$$2Na_4(UO_2)(CO_3)_3 = Na_2U_2O_7 + 3Na_2CO_3 + 3CO_2 \qquad (7)$$

followed at the later stage by

$$Na_2U_2O_7 + Na_2CO_3 = 2Na_2UO_4 + CO_2 \qquad (8)$$

Only part of the sodium carbonate produced in reaction (7) is used in (8), and therefore some will remain in the final product. Its fusion (pure sodium carbonate melts at 850°) accounts for the "shoulder" in the second DTA peak. This shoulder can be observed in isolation as a peak by alternately cooling and re-heating the DTA furnace after the reaction (8) is complete. The agreement between observed and calculated weight losses shown in Table II confirms the correctness of equations (7) and (8). Precision in the observed weight changes is somewhat low because of their poorly defined commencement.

Thermal decomposition of sodium diuranyl pentacarbonate

By an argument similar to that used for SUTC it can be shown that sodium diuranyl pentacarbonate decomposes as follows:

$$Na_6(UO_2)_2(CO_3)_5 = Na_2U_2O_7 + 2Na_2CO_3 + 3CO_2 \qquad (9)$$

$$Na_2U_2O_7 + Na_2CO_3 = 2Na_2UO_4 + CO_2 \qquad (10)$$

The residual sodium carbonate causes a marked fusion peak in the DTA trace.

Thermal decomposition of sodium uranyl dicarbonate

Analogy with SUTC and sodium diuranyl pentacarbonate leads to the equations:

$$2Na_2UO_2(CO_3)_2 = Na_2U_2O_7 + Na_2CO_3 + 3CO_2 \qquad (13)$$

$$Na_2U_2O_7 + Na_2CO_3 = 2Na_2UO_4 + CO_2 \qquad (14)$$

No sodium carbonate remains in excess at the conclusion of these reactions, and no effect attributable to it is seen in the DTA trace.

Thermal decomposition of sodium trioxyuranic diuranyl pentacarbonate

The loss in weight of this compound corresponds to a loss of 4 moles of carbon dioxide per mole of pentacarbonate at the first decomposition stage, and the loss of the remaining one mole at the second stage. By analogy with the cognate materials, this decomposition can be formulated:

$$Na_6(UO_3)_3(UO_2)_2(CO_3)_5 = 2Na_2U_2O_7 + Na_2CO_3 + UO_3 + 4CO_2 \qquad (11)$$

followed by:

$$Na_2U_2O_7 + Na_2CO_3 = 2Na_2UO_4 + CO_2 \qquad (12)$$

No residue of sodium carbonate remains after reaction (12), and no structure attributable to its fusion is observed in the DTA trace.

Analytical evidence for the decomposition reactions

In addition to the support given to the proposed decomposition reactions by observed thermogravimetric weight losses, evidence is obtainable by direct analysis of the residues. Separate quantities of each of the sodium uranyl carbonates were heated in a furnace to temperatures at which the compounds should be half- and fully-reacted, and assayed for uranium and carbon dioxide. If equations (7) and (8), (9) and (10), (11) and (12) and (13) and (14) are compared, it will be seen that in every case a different proportion of uranium and carbonate remains in the residue. Table III compares uranium and carbon dioxide values actually found with those predicted by the proposed equations.

The agreement between calculated and assayed values shown in Table III is sufficient to prove the formulae proposed for the decomposition of each of the compounds considered.

TABLE III

COMPARISON OF CALCULATED AND ASSAYED URANIUM AND CARBON DIOXIDE VALUES IN SODIUM URANYL CARBONATE DECOMPOSITION RESIDUES

Compound	*Residual U Values, Percentage*				*Residual CO_2 Values, Percentage*			
	Half Decomposed		*Fully Decomposed*		*Half Decomposed*		*Fully Decomposed*	
	Calc.	*Assayed*	*Calc.*	*Assayed*	*Calc.*	*Assayed*	*Calc.*	*Assayed*
$Na_4(UO_2)(CO_3)_3$ (SUTC)	50.2	48.4	52.4	53.8	13.9	14.4	9.70	5.84
$Na_6(UO_2)_2(CO_3)_5$	56.3	52.8	59.3	57.6	10.4	12.2	5.49	5.36
$Na_6(UO_2)_2(UO_3)_3(CO_3)_5$	71.6	76.0	73.5	73.0	2.65	2.33	zero	n.d.[a]
$Na_2UO_2(CO_3)_2$	64.3	63.2	68.4	67.2	5.94	6.80	zero	n.d.[a]

[a] not detected

SUMMARY

The thermal decomposition of the sodium uranyl carbonates and the binary uranyl carbonate, has been investigated by differential thermal analysis and thermogravimetry. Uranyl carbonate decomposes in one stage only: $UO_2CO_3 = UO_3 + CO_2$. Evidence was obtained for a two-stage thermal decomposition, of the sodium uranyl carbonates, following the equations:

$2Na_4UO_2(CO_3)_3$ sodium uranyl tricarbonate	$= Na_2U_2O_7 + 3Na_2CO_3 + 3CO_2$ sodium diuranate	$= 2Na_2UO_4 + 2Na_2CO_3 + CO_2$ sodium uranate
$2Na_2UO_2(CO_3)_2$ sodium uranyl dicarbonate	$= Na_2U_2O_7 + Na_2CO_3 + 3CO_2$	$= 2Na_2UO_4 + CO_2$
$Na_6(UO_2)_2(CO_3)_5$ sodium diuranyl pentacarbonate	$= Na_2U_2O_7 + 2Na_2CO_3 + 3CO_2$	$= 2Na_2UO_4 + Na_2CO_3 + CO_2$
$Na_6(UO_2)_2(UO_3)_3(CO_3)_5$ sodium trioxyuranic diuranyl pentacarbonate	$= 2Na_2U_2O_7 + Na_2CO_3 + UO_3 + 4CO_2$	$= Na_2UO_4 + 2Na_2U_2O_7 + CO_2$

RÉSUMÉ

Une étude a été effectuée sur la décomposition thermique du carbonate d'uranyle et des uranylcarbonates de sodium.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die thermische Zersetzung von Uranylcarbonat und Natrium-uranylcarbonat.

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SEMIMICRO MANOMETRIC METHOD FOR THE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS

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The analysis of organic compounds for carbon and hydrogen continues to be among those in greatest demand in many petroleum and petrochemicals research laboratories. Increasing demands for carbon and hydrogen analyses in this laboratory necessitated a search for a faster, more accurate and more stable method than the conventional semimicro gravimetric method used for the past several years.

Lack of a temperature and humidity-controlled balance room, plus the inherent difficulties associated with weighing micro absorbers influenced our decision against the rapid microgravimetric methods, such as those of CLARK[1] and ROBERTSON *et al.*[2]. WHITE *et al.*[3] reported excellent accuracy and speed using an automatic macrocombustion-gravimetric method, but the necessary 0.2-g sample is frequently not available in our laboratory. UNTERZAUCHER[4] and JOHANSSON[5] have published methods in which the water and carbon dioxide from a conventional microcombustion are determined volumetrically.

NAUGHTON AND FRODYMA[6], and SCHÖNIGER[7] have described methods in which the water and carbon dioxide from a combustion are measured manometrically. Although their methods do not offer any substantial improvements in accuracy over the gravimetric procedure, they do feature the desired speed and the potential for good stability and accuracy. Each of these methods involves the use of a two-liquid manometer. Observations made in this laboratory during use of a two-liquid manometer indicate several reasons for variations in results. In order to correct for these variations, major innovations were made in the manometer system. The two-liquid manometer was abandoned, and an entirely new mercury manometer designed which is immersed in a bath maintained at a constant elevated temperature.

In the method finally developed, combustion of the sample is accomplished in a modified Pregl apparatus which utilizes an automatically controlled gas sample heater. Water and carbon dioxide are collected in dry ice and liquid nitrogen traps, respectively, and selectively vaporized into an evacuated manometer immersed in a constant temperature bath. The observed pressure of each component is referred to a calibration curve to determine the amounts of carbon and hydrogen present. Nitrogen oxides are removed from the combustion gases by adsorption on activated manganese dioxide in an external scrubber.

Specifically, the method described offers the following features which have been found in this laboratory to be requirements for highly accurate manometric carbon and hydrogen determinations:

(1) The mercury manometer eliminates the troublesome oil drainage problems of a two-liquid manometer, and affords a three-fold increase in the total pressure that can be observed. Manometer readings are facilitated by use of an accurate steel centimeter scale and vernier and a simple device for observing the mercury meniscus made from a slide rule magnifier.

(2) The use of an elevated temperature (70°) in the manometer bath enables the analyst to select sample size for optimum pressure deflection without danger of water vapor condensation in the manometer, and affords a ten-fold increase in pressure readings for water vapor. Maintenance of the temperature within $\pm$ 0.02° prevents variations in observed pressures caused by changes in room temperatures.

(3) Calibration curves are used for converting observed pressures to weights of water and carbon dioxide because the calibration factors for the manometer were found to vary at different pressures.

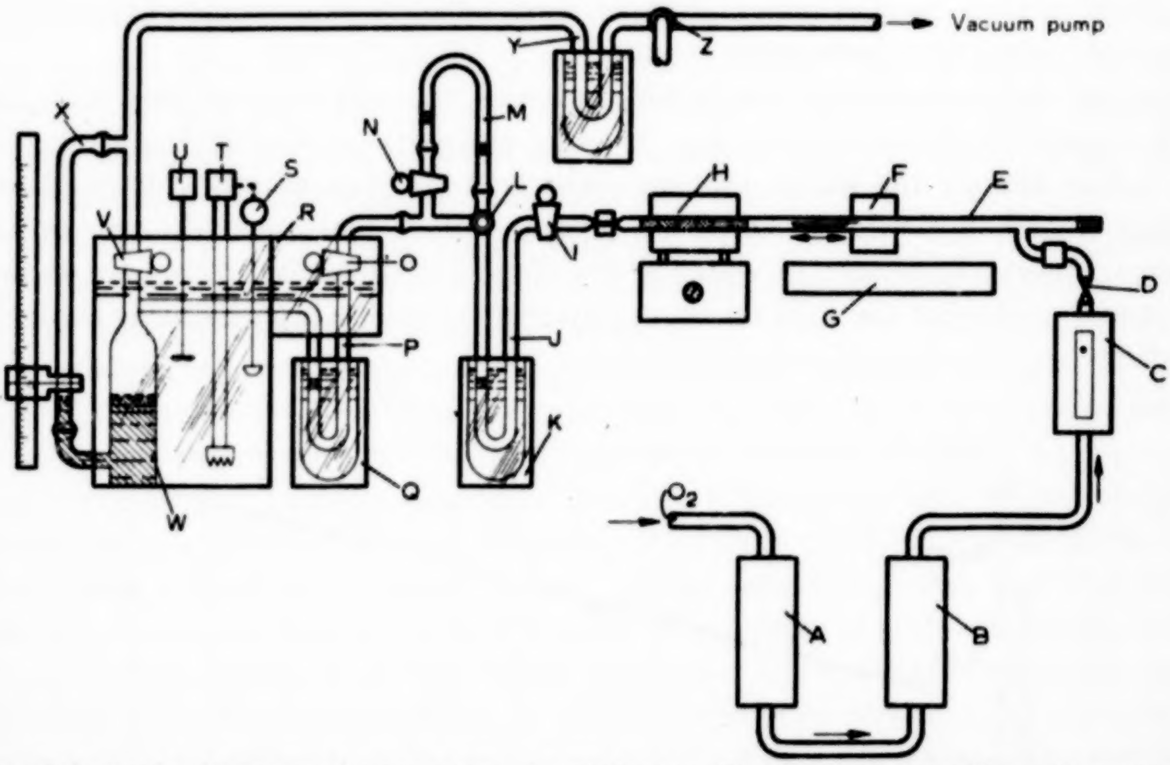

Fig. 1. Schematic diagram of apparatus. A, preheater; B, CO_2–H_2O scrubber; C, rotameter; D, oxygen valve; E, combustion tube; F, gas sample burner; G, automatic drive unit; H, electric micro furnace; I, stopcock; J, water trap; K, dewar flask; L, 3-way stopcock; M, nitrogen oxides scrubber; N, stopcock; O, flow rate stopcock; P, carbon dioxide trap; Q, dewar flask; R, manometer bath; S, thermostat; T, immersion heater; U, stirrer; V, differential stopcock; W, mercury; X, manometer; Y, pump protector trap; Z, 3-way stopcock.

Apparatus

A schematic diagram of the apparatus is shown in Fig. 1. The letter below refers to the identification of the item in Fig. 1. (A) Preheater – the conventional copper oxide-filled, electrically-heated, micro unit is satisfactory. (B) Carbon dioxide–water scrubber – any scrubbing tower that will hold 50 g of Ascarite and 50 g of magnesium perchlorate is satisfactory. (C) Rotameter – Brooks-Mite purge meter No. 2022-V, size 1 (Brooks Rotameter Company, Lansdale, Pennsylvania). (D) Oxygen valve – needle valve for control of oxygen flow. (E) Combustion tube – standard Vycor combustion tubes with side arm are modified by lengthening about 6 in. (F) Sample burner – a single, concentric, gas-fired, elliptical-shaped burner of special design is used to heat both combustion tubes simultaneously. (G) Automatic drive unit. (H) Electric micro furnace – Fisher improved microbustion furnace No. 20-288 (Fisher Scientific Co., St. Louis). Two tubes can be heated by a single furnace if the holes in the end of the case are enlarged slightly. (I, N.) Stopcocks. (J) Water trap – equipped with a coarse porosity fritted glass disk. The traps should be sufficiently compact for two traps to fit into a 1-pint Dewar flask. (K, Q) Dewar flasks. (L, Z) Three-way stopcocks. (M) Nitrogen oxides scrubber – filled with Leco special grade manganese dioxide (Laboratory Equipment Co., St. Joseph, Michigan). Small sections of magnesium perchlorate are placed in both ends of the scrubber. (O) Flow rate stopcock. (P) Carbon dioxide trap. (R) Manometer bath – filled with water and covered with a 1/8-in. layer of mineral oil to reduce evaporation. Either glass or metal may be used. (S) Thermostat – capable of regulating the temperature of water in the bath to 70 ± 0.02°. (T) Immersion heater. (U) Heavy duty stirrer. (Y) Pump protector trap.

Reagents and materials

Atlantic hard cement – (Alexander Glass-blowing Service, Philadelphia, Pa.). Benzoic acid – N.B.S. certified grade. Copper oxide – 20 to 40 mesh. Liquid nitrogen. Oxygen. Platinized asbestos. Platinum gauze – 100 mesh. Silver gauze – 20 mesh.

Procedure

Condition freshly-filled combustion tubes by heating (800°–850°) overnight in a stream of oxygen. Warm the end of the combustion tube with a flexible heating tape to prevent condensation of water. Burn an unweighed 10-mg sample of benzoic acid, but do not collect the combustion products.

Calibrate the manometers by burning a series of accurately-weighed samples of N.B.S. benzoic acid from 5 to 25 mg. Measure and record the resulting pressures for both carbon dioxide and water. Plot mg carbon per cm of carbon dioxide *vs.* observed pressure of carbon dioxide in cm. On a separate sheet, plot mg hydrogen per cm of water *vs.* observed pressure of water in cm. Typical calibration curves are shown in Figs. 2 and 3. Repeat the calibration approximately once a month during continuous operation.

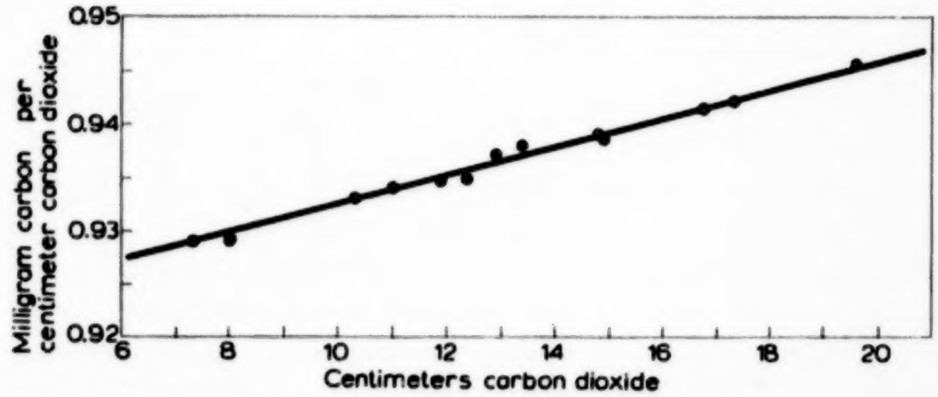

Fig. 2. Typical calibration curve for carbon.

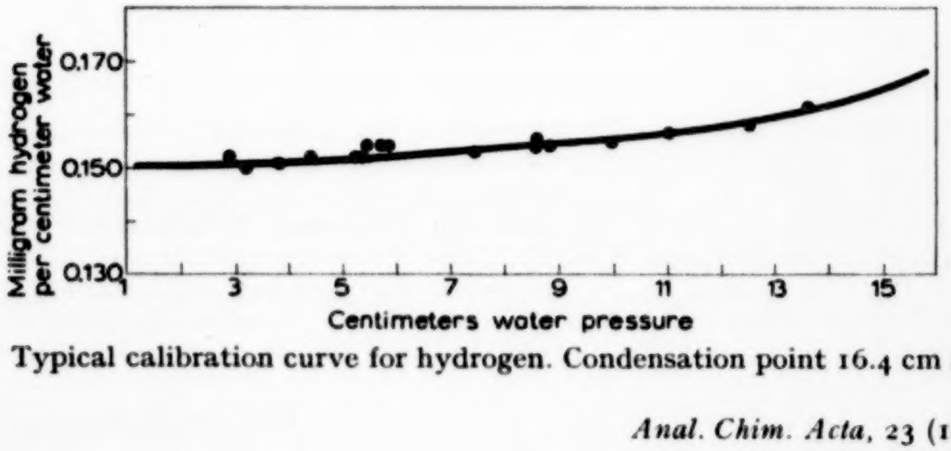

Fig. 3. Typical calibration curve for hydrogen. Condensation point 16.4 cm at 62°.

Choose a weight of sample, based on the expected carbon content, that will give an optimum manometer reading. Weigh samples into a platinum boat accurately to ± 0.01 mg. With the furnace at 800–850°, close stopcock I and open stopcocks L, N, O and V. Place a dewar flask filled with liquid nitrogen on vacuum line trap Y, and then open stopcock Z to the vacuum pump.

Caution: The vacuum line trap Y must remain under vacuum whenever it is immersed in liquid nitrogen in order to prevent condensation of oxygen in the trap.

Quickly insert the sample boat in the combustion tube to a position 4 in from the furnace. Close stopcock O and open I. Place a dewar flask filled with liquid nitrogen on the carbon dioxide trap P, and a dewar filled with dry ice and acetone on water trap J. With valve D opened wide, adjust stopcock O to give an oxygen flow rate of 10 to 20 ml per min. Place the sample burner 3 in behind the sample boat and light the burner. Set the automatic drive unit so that the burner will complete its cycle in 10 to 20 min. After completion of the combustion increase the oxygen flow to 40 ml per min and sweep out the system for 10 min.

Close stopcock O and evacuate the manometer until no rise is observed in the mercury level in the manometer arm when stopcock V is closed. One or two min of pumping is usually sufficient. Close stopcock V and replace the dewar flask containing liquid nitrogen with one filled with boiling water. Increase the voltage to the immersion heater in the water when the water ceases to boil; reduce the voltage when boiling reoccurs. When the mercury level has ceased to rise, aided by gently tapping, read the level to the nearest 0.001 cm and record.

Open stopcock V and pump off the carbon dioxide. Replace the dewar flask containing boiling water with one filled with liquid nitrogen. Open stopcock O, close N, and turn L to bypass the nitrogen oxides scrubber. Replace the dewar flask filled with dry ice and acetone with one containing boiling water. Allow 3 to 5 min for vaporization of the water into the liquid nitrogen trap. Vaporize the water into the manometer and read the pressure as described for carbon dioxide. Read the pressure of the water vapor as rapidly as possible after reaching a maximum (the pressure begins to diminish because of adsorption on the glass). Open stopcock V and pump off the water.

Determine a blank in the same manner, except omit the sample and continue the sweep-out for several hours. Divide the total carbon dioxide and water deflections by the appropriate factor to obtain blank values for the normal combustion period. Redetermine the blank occasionally to test the efficiency of the oxygen purification system and the condition of the combustion tube filling. A normal blank is so low (less than 10 μg) and constant that it is of very small significance in the calculations.

Calculations

$$\text{Wt.\% carbon} = \frac{(P_c - B_c)\,(F_c)\,100}{W}$$

$$\text{Wt.\% hydrogen} = \frac{(P_h - B_h)\,(F_h)\,100}{W}$$

Where: P_c, P_h = Observed pressures (in cm) of carbon dioxide and water, respectively.
B_c, B_h = Blanks (in cm) of carbon dioxide and water, respectively.
F_c = Factor, mg carbon per cm of observed CO_2 pressure, obtained from CO_2 calibration curve.
F_h = Factor, mg hydrogen per cm of observed water vapor pressure obtained from hydrogen calibration curve.
W = Weight of sample in mg.

Precautions

The flow rate of oxygen through the system must allow sufficient time for condensation of the combustion products in the liquid nitrogen traps, in order to prevent loss of carbon dioxide and water. It is also imperative that the U-traps be equipped with coarse fritted glass disks to avoid loss of small, solid frozen particles. It is equally important that these disks remain under the liquid nitrogen and that they are located on the outlet side of the trap. Solid particles normally are blown against the disks and if the disk is above the liquid nitrogen serious loss of carbon dioxide will result.

Adsorption of water on the glass surfaces of the manometer causes some difficulty. The maximum reading for the water pressure must be obtained rapidly, before it begins to diminish because of adsorption effects. The rate of decrease in the water pressure can be reduced effectively by coating the inside of the manometer with a silicone product sold under the trade name "Siliclad".

RESULTS

Data from the analysis of five compounds of known purity are shown in Table I. These data are from consecutive determinations with no values omitted. The precision attainable on typical routine samples is illustrated in Table II. Using the dual apparatus described and a semimicro sample weighed to ± 0.01 mg, 16 determinations are normally made in an eight-hour day.

TABLE I

ANALYSIS OF COMPOUNDS OF KNOWN PURITY

Compound	*Elements present*	*% Carbon*		*% Hydrogen*	
		Theory	*Found*	*Theory*	*Found*
Benzoic acid	C,H,O	68.84	68.78	4.95	4.91
			68.90		4.93
			68.98		4.97
			68.81		5.03
			68.83		4.93
			68.78		4.93
Anisic acid	C,H,O	63.18	63.17	5.26	5.28
			63.15		5.42
			63.30		5.30
			63.18		5.26
Chlorobenzoic acid	C,H,O,Cl	53.70	53.69	3.22	3.22
			53.73		3.22
			53.76		3.22
Tri-α-naphthyl phosphate	C,H,O,P	75.65	75.65	4.41	4.44
			75.59		4.45
Cystine	C,H,O,N,S	29.99	30.06	4.99	5.02
			29.99		5.04
			30.03		5.02
Average deviation			±0.05		±.03
Maximum deviation			±0.14		±0.16

TABLE II

ANALYSIS OF TYPICAL ROUTINE SAMPLES

Sample	*Elements present*	*% Carbon*	*% Hydrogen*
Research compound A	C,H,O,Cl,N	15.35 15.15	6.02 5.90
Polymer X	C,H,O,N	41.15 41.08	4.81 4.72
Research compound B	C,H,O,N,S	30.07 30.00	4.28 4.22
Polymer Y	C,H,O	82.89 83.20	10.58 10.56
Research compound C	C,H,O,N,S,Cl	6.28 6.43	3.40 3.18
Polymer Z	C,H,O	87.68 87.88	10.58 10.36
Research compound D (about 55% Cl)	C,H,Cl	40.83 40.89	3.16 3.16
Average deviation from mean		±0.07	±0.05

SUMMARY

A manometric method for determination of carbon and hydrogen is described which affords significant improvements in accuracy over both previously reported manometric techniques and the conventional Pregl gravimetric method. Water and carbon dioxide from the combustion are collected in dry ice and liquid nitrogen traps, respectively, and selectively vaporized into an evacuated mercury manometer immersed in a bath maintained at a constant elevated temperature. The observed pressure of each component is referred to a calibration curve to determine carbon and hydrogen. Nitrogen oxides are removed by adsorption on activated manganese dioxide in an external scrubber.

RÉSUMÉ

Une semicro méthode manométrique est décrite pour le dosage du carbone et de l'hydrogène. L'eau et l'anhydride carbonique provenant de la combustion sont recueillis respectivement dans de la glace sèche et dans de l'azote liquide; ils sont ensuite vaporisés dans un manomètre. La précision obtenue est meilleure que celle obtenue avec les méthodes manométriques habituelles ou la méthode gravimétrique de Pregl.

ZUSAMMENFASSUNG

Beschreibung einer manometrischen Halbmikromethode zur Bestimmung von Kohlenstoff und Wasserstoff. Das bei der Verbrennung gebildete Wasser sowie das Kohlendioxyd werden getrennt ausgefroren und dann selektiv in ein evakuiertes Quecksilbermanometer verdampft. Aus der Druckänderung kann dann der Gehalt an Kohlenstoff und Wasserstoff berechnet bezw. an einer Kalibrationskurve abgelesen werden.

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SPECTROPHOTOMETRIC DETERMINATION OF INDIUM WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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INTRODUCTION

Although several colorimetric methods have been described for the determination of indium[1-5], the colour reactions are not very sensitive. This paper reports a new, sensitive and selective analytical procedure. 1-(2-Pyridylazo)-2-naphthol(PAN) reacts with many heavy metals to form red chelates[6-13]. Indium forms a red chelate under acidic conditions. In chloroform solution the indium chelate has absorbance maxima at 530 and 560 mμ approximately. Chelation with the reagent is the basis of a simple colorimetric method for the determination of indium. The method has been applied to zinc residues.

EXPERIMENTAL

Apparatus and reagents

All measurements were made with a Model EPV-2 Hitachi spectrophotometer, using 1-cm cells. A Beckman H-2 type pH meter was used.

Standard solution of indium: This solution was prepared by dissolving 1.100 g of pure metal (99.9%) in small amounts of hydrochloric acid and diluting to 1 l. It was standardized by the gravimetric method.

Standard solution of iron: A solution was prepared containing 1.00 mg of iron per ml by dissolving standard iron wire in hydrochloric acid.

1-(2-*Pyridylazo*)-2-*naphthol solution:* A 0.1% solution was prepared by dissolving 100 mg of PAN (Tokyo Kasei Chem. Co.) in absolute methanol, filtering through glass wool, and diluting to 100 ml with methanol. This solution is stable for several weeks if stored in an amber bottle.

Buffer solution: The pH was adjusted by adding a mixed solution of sodium acetate–acetic acid.

All other chemicals used in this work were pure Wako's reagents.

Procedure

An aliquot of the slightly acid or neutral solution containing up to 50 μg of indium (diluted to approximately 20 ml) was mixed with 1 ml of 0.1% dye soliution and 5 ml of the buffer solution (pH 5.4–6.7) and allowed to stand for 5 min. Exactly 10.0 ml of chloroform was added to the mixture which was then shaken vigorously for 1–2 min. The chloroform extract was centrifuged and the absorbance measured at 560 mμ against the reagent blank. The concentration of indium was found by means of a calibration curve, using known amounts of indium.

RESULTS AND DISCUSSION

Absorption curves. The absorption curves of the indium complex with PAN and the iron complex with PAN over the spectral range of 850–500 mμ are shown in Fig. 1.

Beer's law. The indium–PAN complex followed Beer's law in the range 0–50 μg of indium in 10 ml of chloroform when the absorbance was measured at 560 mμ (Fig. 2).

Effect of pH. Solutions containing indium and PAN were adjusted to various pH values with sodium acetate–acetic acid or ammonium chloride–ammonia buffer solutions. Between pH 5.3 and 6.7 the absorption remained approximately constant (Fig. 3).

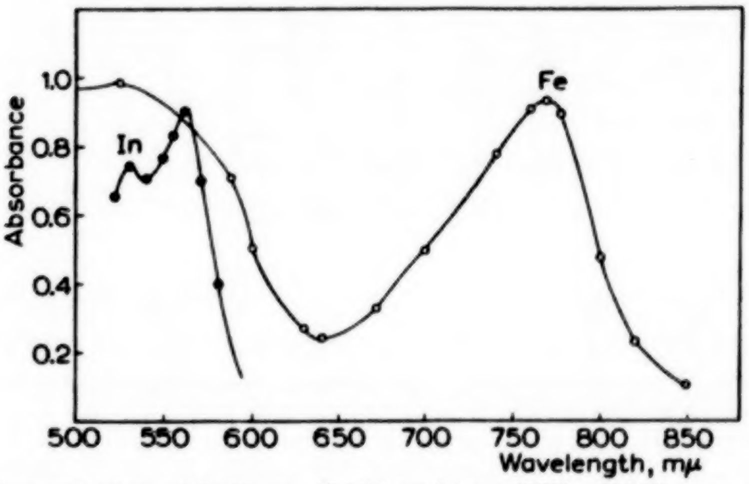

Fig. 1. Absorption spectra of indium–PAN and iron(III)–PAN complexes in chloroform.

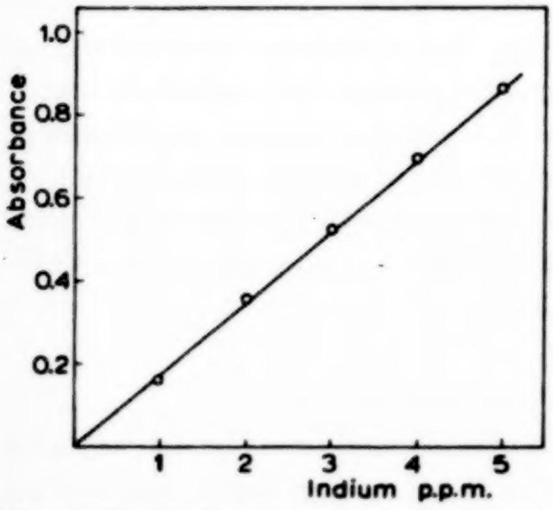

Fig. 2. Beer's law. pH 5.5, $\lambda = 560$ mμ.

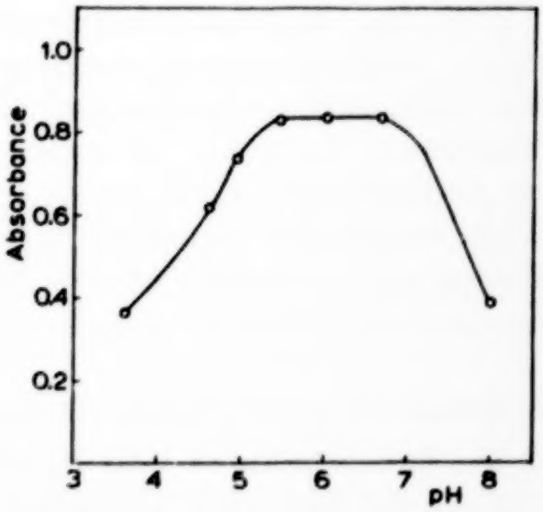

Fig. 3. Effect of pH on absorbance of chloroform extract. 48 μg indium, $\lambda = 560$ mμ.

Solvent for extraction. Both PAN and the indium chelate of PAN were soluble in chloroform or isoamylalcohol. Chloroform was the more efficient solvent.

Sensitivity. The molar extinction coefficient of the indium–PAN chelate was calculated to be 19600 from Beer's law. The sensitivity of the colour reaction was 0.0058 μg/cm² according to Sandell's definition.

Time of standing and stability of colour. Fig. 4 shows that the minimum time for complete colour development of the indium–PAN chelate was five minutes. The chloroform solution of indium–PAN chelate was stable for several hours after preparation.

Effect of dye. 1 ml of 0.1% dye solution was satisfactory for up to 50 μg of indium.

Composition of the complex. The empirical formula of the coloured complex of indium was determined by means of the mole ratio method (Fig. 5). Within experimental error the results suggest a 1 : 2 complex of indium with PAN.

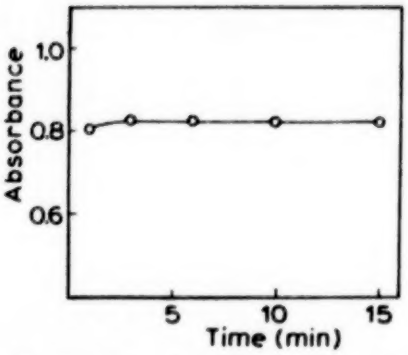

Fig. 4. Variation of absorbance with time. 48 μg indium, pH 5.5, λ = 560 mμ.

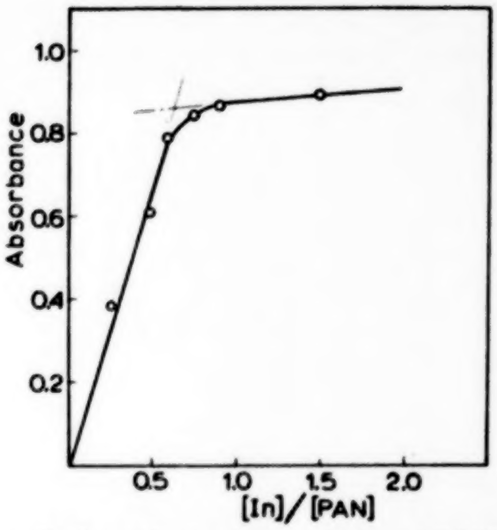

Fig. 5. Mole-ratio method. [In] = [PAN] = $3.55 \cdot 10^{-3}$ *M*, pH 5.5, λ = 560 mμ.

Interferences

Citric and tartaric acid interfered with the colour development. Chloride, bromide, iodide, sulphate, nitrate, carbonate, and acetate as their sodium, potassium, or ammonium salts did not interfere. Iron, zinc, copper, and gallium interfered strongly. Aluminium, beryllium, manganese, lead, titanium and small amounts of bismuth, tin, and cadmium did not interfere. The strong interferences of copper and zinc would not be expected to occur if the hydroxide separation technique was used in an analysis. The strong interference of iron can be avoided by means of a simultaneous determination (see below).

Simultaneous spectrophotometric determination of indium and iron

The ferric chelate of PAN in chloroform has two absorbance maxima at 525 and 775 mμ, and Beer's law is obeyed at both wavelengths. On the other hand, the indium chelate has no absorption at 775 mμ. Therefore, both indium and iron can be determined simultaneously by the procedure given above, if the absorbances are measured at 560 and 775 mμ and the following formulas are applied (see Table I).

$$C_{\mathrm{Fe}} = \frac{A_{775}}{a^{\mathrm{Fe}}_{775}}$$

$$C_{\mathrm{In}} = \frac{a^{\mathrm{Fe}}_{775} \cdot A_{560} - a^{\mathrm{Fe}}_{560} \cdot A_{775}}{a^{\mathrm{In}}_{560} \cdot a^{\mathrm{Fe}}_{775}}$$

where C_{Fe} and C_{In}: iron and indium present in μg, A_{560} and A_{775}: absorbances measured at 560 and 775 mμ. a^{In}_{560}, a^{Fe}_{560}, a^{Fe}_{775}: absorbancy index of indium and iron at 560 and 775 mμ.

TABLE I

SIMULTANEOUS DETERMINATION OF INDIUM AND IRON

Taken (μg)		*Found (μg)*	
indium	*iron*	*indium*	*iron*
10.0	8.3	10.0	8.3
10.0	16.6	10.1	16.7
10.0	24.9	10.0	25.0
10.0	33.2	10.4	33.5
10.0	41.6	10.2	42.0

In these experiments the value of these absorbancy indexes obtained were as follows: $a_{560}^{Fe} = 0.028$, $a_{775}^{Fe} = 0.029$, $a_{560}^{In} = 0.0172$.

Analysis of zinc residue

Transfer 1.000 g of the zinc residue to a 500-ml beaker. Add 20 ml of mixed acid. Cover and heat gently until dissolution of the sample is complete, then add an excess of sulphuric acid and evaporate the solution to fumes of sulphur trioxide. Cool and dilute to 300 ml. Treat the solution with excess of ammonium hydroxide solution. Dissolve the precipitate in hydrochloric acid to remove copper and other interfering metals by the method of BAYER[14]. Filter the precipitate (iron and indium), and wash with weak ammonium hydroxide solution; then dissolve in hydrochloric acid. Transfer to a 100-ml volumetric flask, and dilute to the mark with distilled water. Transfer a 2- to 5-ml aliquot of the sample to a separation funnel and analyze according to the procedure (see Table II).

TABLE II

ANALYSIS OF ZINC RESIDUES(%)

PAN method	*Polarographic method*	*Neothoron method*[15]
0.014	0.014	0.014
0.014	0.014	0.013

SUMMARY

A spectrophotometric method for a rapid determination of indium and simultaneous determination of indium and iron with 1-(2-pyridylazo)-2-naphthol is described.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage de l'indium et du fer, au moyen du (pyridylazo-2)-1-naphthol-2.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Indium und Eisen mit Hilfe von 1-(2-Pyridylazo)-2-naphtol.

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ION-EXCHANGE SEPARATION OF TITANIUM FROM STEELS AND ITS DETERMINATION WITH HYDROGEN PEROXIDE[*]

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INTRODUCTION

If titanium is to be determined in steels by the usual peroxide method, it must be separated from associated ions[1]. The present paper deals with the ion-exchange separation of titanium as a fluoride complex before its determination with hydrogen peroxide.

EXPERIMENTAL

Titanium solution: Titania was dissolved by treating with hydrofluoric and hydrochloric acids. The final solution was 0.04 *N* in hydrofluoric acid and 0.02 *N* in hydrochloric acid. The TiO_2 content was found to be 0.53 mg Ti/ml.

Anion-exchange resin: Amberlite IRA-400 (0.4–0.6 mm diam., chloride form) was used as a column of 1.0 cm diameter and 6 cm height in a polythene apparatus.

All other reagents were of C.P. grade.

WOODS AND COCKERELL[2] studied the distribution of titanium on an anion-exchange resin in the presence of hydrofluoric acid. With the present column quantitative exchange and retention of titanium was studied by passing a solution containing about 0.5 mg of titanium mixed with varying concentrations of hydrofluoric and hydrochloric acids through the column at a flow rate of about 2.5 ml per min and then washing the column with 100 ml of the same mixtures of acids (without titanium). The titanium retained on the column was eluted with 50 ml of 3 *N* hydrochloric acid at the same flow rate and determined by the usual peroxide method. The effect of variation of the composition of the two acids on the separation of titanium from iron was also studied (Table I). Experiments No. 1–5 show quantitative retention of titanium up to 1 *N* hydrofluoric acid provided that the hydrochloric acid concentration does not exceed 0.2 *N*. No interference from iron was found under the conditions of quantitative retention of titanium (Expts. 6–15).

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[*] Presented to the 47th Session of the Indian Science Congress.

In experiment 6 the iron in the effluent was determined and found to be 0.199 g indicating a quantitative separation.

The behaviour of other materials in steels was studied at a concentration of 0.4 *N* hydrofluoric acid and 0.1 *N* hydrochloric acid. The nature and quantity of these substances were as follows:

Chromium chloride, 36 mg Cr, nickel chloride, 16 mg Ni, ammonium vanadate, 2.2 mg V, ammonium molybdate, 3.0 mg Mo, cobalt chloride, 10 mg Co, manganese chloride, 10 mg Mn, sodium tungstate, 10 mg W, niobium and tantalum fluorides, 4.0 and 2.0 mg metal.

TABLE I

EFFECTS OF VARIATION OF COMPOSITION OF HYDROCHLORIC AND HYDROFLUORIC ACIDS ON THE RETENTION OF TITANIUM ON THE RESIN COLUMN

Titanium taken in each experiment = 0.53 mg; iron added in experiments 6–15 = 0.2 g

Expt. No.	*Normality of hydrochloric acid*	*Normality of hydrofluoric acid*	*Retention of titanium %*
1	0.02	0.08	100
2	0.2	0.4	100
3	0.2	1.0	100
4	0.3	0.4	92
5	0.3	1.0	43.7
6	0.1	0.2	100
7	0.1	0.4	100
8	0.1	1.0	100
9	0.2	0.5	100
10	0.3	0.5	65
11	0.4	0.2	53
12	0.4	0.4	49
13	0.4	1.0	46
14	0.8	0.2	0
15	0.8	0.4	0

The added element was not estimated in the effluent. Vanadium was found to be partially retained along with titanium; on increasing the volume of the wash liquid to 200 ml, the retained vanadium alone was completely eluted. Even when 600 ml of wash liquid was used as the eluent, no titanium was eluted.

To elute the titanium, different concentrations of hydrochloric acid were tested.

TABLE II

STUDIES OF ELUTION OF TITANIUM

Titanium taken 2.1 mg

Normality of HCl	*Volume of HCl*	*% Titanium eluted*
1.0	50 ml	100
1.0	25 ml	88.9
2.0	25 ml	89.0
3.0	25 ml	100

A minimum of 25 ml of 3 *N* acid was found to be necessary for quantitative elution at a flow rate of 2.5 ml/min.

By means of the procedure given below, standard samples were analysed; the results are recorded in Table III.

PROCEDURE

Take 0.2 g of steel sample in a 100-ml beaker, and dissolve in 10 ml of concentrated hydrochloricd aci and a few drops of nitric acid. Evaporate to dryness on a water bath. Add 2 ml of concentrated hydrochloric acid, transfer the solutions with washings to a 250-ml polythene beaker, and add 4 ml of 40% hydrofluoric acid. Dilute the solution to 200 ml. Pass this solution through the resin column (Amberlite IRA-400) at a flow rate of 2.5 ml/min. Wash the column with 200 ml of wash liquid (2 ml of hydrochloric acid and 4 ml of hydrofluoric acid diluted to 200 ml) and then with 50 ml of water. Elute the titanium with 25 ml of 3 *N* hydrochloric acid at the same flow rate, and wash with 50 ml of distilled water. To the effluent, add 10 ml of 1 : 1 sulphuric acid, and fume thoroughly. Dilute the solution to about 40 ml, add 1 ml of 30 vol. hydrogen peroxide, transfer to a 50-ml volumetric flask, and dilute to volume. Measure the optical density at 425 mμ. From a calibration curve, compute the titanium content of the sample.

TABLE III

ANALYSIS OF SAMPLES

No.	*Sample*	*Ti present* %	*Ti found* %	*Difference Ti in* %
1.	B.C.S. No. 235 stainless steel	0.62	0.63	+0.01
2.	B.C.S. No. 233 permanent magnet alloy	0.79	0.80	+0.01
3.	B.C.S. No. 206 cast iron	0.16	0.18	+0.02
4.	B.C.S. No. 236/1 hematite iron	0.065	0.066	+0.001
5.	Sample serial No. 3562	0.30[a]	0.32	+0.02

[a] Analysed by the method given in Ref.[1]

SUMMARY

Titanium is quantitatively separated from its associated elements in steels as the fluoride complex on an anion-exchange resin, and can be determined by the usual peroxide method.

RÉSUMÉ

Les auteurs décrivent une séparation du titane dans les aciers, en utilisant une résine échangeur d'anions. Le titane est finalement dosé par la méthode habituelle au peroxyde d'hydrogène.

ZUSAMMENFASSUNG

Beschreibung eines Verfahrens zur Abtrennung von Titan in Stahl mit Hilfe eines Jonenaustauschers. Die Bestimmung des Titans erfolgt nach der Wasserstoffperoxyd-Methode.

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CATION-EXCHANGE BEHAVIOUR OF BARIUM ON DOWEX 50W-X8

SEPARATION FROM MIXTURES

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As one of the major constituents of fission products, barium has attracted considerable attention in recent years. Several ion-exchange methods have been applied to barium in this laboratory[1-3]. Ion-exchange separations of barium from various elements, *e.g.* lead, strontium, radium and lanthanum, have been effected by different workers[4-10].

MINAMI AND ISHIMORI[4] explored the possibility of separating barium from lead on a cation-exchanger by first eluting the adsorbed lead with ammonium acetate at pH 6.0 and then barium with 10% ammonium chloride. The difference in the stability of the anionic complexes of barium and lead with ethylenediaminetetraacetic acid at pH 4.5 and 10.5 respectively has been utilised for their separation[5]; lead (pH 4.5) passed out of bed and the adsorbed barium was eluted with ethylenediaminetetraacetic acid (disodium salt) at pH 10.5. The anion-exchange separation[6] of lead from barium has been effected by adsorbing the anionic lead chloride complex on an anionite while barium passed through. The separation of barium from strontium has been done by BOVY AND DUYCKAERTS[7]; the metals were eluted selectively with EDTA at varying pH. A direct method has been devised[8,9] for the separation of barium from radium using 0.5 *M* ammonium citrate solution adjusted to pH 7.5–8.0. Selective elution with 5% citric acid at pH *ca.* 4.0 permits the separation of lanthanum from barium[10].

However, systematic cation-exchange studies of barium have not been reported so far. The objective of this investigation was to carry out exploratory studies on the cation-exchange behaviour of barium on Dowex 50W-X8 (hydrogen form). In the present paper nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, sodium chloride, ammonium acetate, citric acid, tartaric acid and EDTA have been studied as the eluting agents. Barium has been separated from uranium(VI), copper(II), mercury(II), caesium, zinc, cadmium, silver, cerium(IV), zirconium, thorium, iron(III) and bismuth(III).

EXPERIMENTAL

Apparatus

Ion-exchange column and Cambridge pH indicator. The ion-exchange column was similar to that described previously[1-3]. A resin bed 1.4 × 20 cm was used.

Reagents

Barium nitrate solution (5 mg Ba/ml). 4.6115 g of barium nitrate (E. Merck) was dissolved in 500 ml of distilled water. The solution was standardised by the chromate method[11]. Dowex

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50W-X8 (Dow Chemical Co., Midland, Mich. U.S.A.), 50–100 mesh (hydrogen form) cation-exchange resin. The resin was treated as before[3].

Chemicals used were all of reagent grade, unless otherwise mentioned.

RESULTS AND DISCUSSION

Ion-exchange studies

An aliquot of barium nitrate solution containing 29.1 mg of barium was passed through the column at a rate of 2 ml per minute. The resin was washed with 50 ml of water and barium eluted with 200 ml of the different eluants. In each case the eluate was collected in 50-ml fractions. In case of mineral acid eluants each fraction was evaporated to dryness; the resulting mass was taken up with 10 ml of water and barium was estimated iodometrically[11]. With salt eluants barium was directly precipitated from the effluent fractions as barium chromate and determined iodometrically.

The elution constant (E) for each eluting agent was calculated as before[1] and an additional correction[3] of 7 ml was made in order to allow for the volume of the solution from the bottom of the resin bed to the tip of the delivery tube. From the values of elution constants the bed distribution coefficient (D) (barium per ml bed/barium per ml solution) was computed by using the relationship[12,13]:

$$D = \frac{1}{E} = \frac{\text{Effluent volume to peak} - \text{free column volume}}{\text{Bed volume}}$$

The results are shown in Table I. The elution behaviour with respect to nitric acid, hydrochloric acid and sodium nitrate, are illustrated as histograms in Fig. 1; elution curves are drawn through the midpoints on the histograms. With 200 ml of nitric acid (2–4 M), hydrochloric acid (3–4 M), sodium nitrate (2–3 M), ammonium chloride (4 M), sodium chloride (4 M) or ammonium acetate (4 M) as eluant barium can be recovered quantitatively. Where the elution peak was observed in some fraction other than the first, that particular fraction was further collected as two 25-ml portions to trace the exact position of the peak (*e.g.* with mineral acids as eluants). When the peak was observed in the first fraction (50 ml), it invariably appeared in the second 25-ml fraction of this portion since the first 17.37 ml of the effluent was due to the free column volume along with extra liquid in the column[3]. The elution constants and the bed distribution coefficients give a measure of the relative efficiency of various eluting agents (Table I). The eluting agents can be arranged in order of increasing

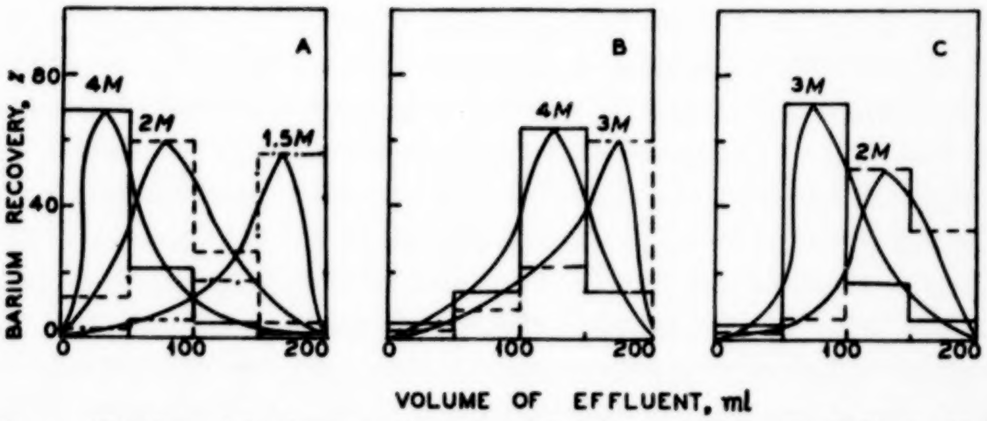

Fig. 1. Elution of barium on Dowex 50W-X8. A–HNO_3; B–HCl; C–$NaNO_3$.

TABLE I

BEHAVIOUR OF BARIUM TOWARDS VARIOUS ELUTING AGENTS

Barium = 29.1 mg. Weight of oven dried resin = 16.3236 g

No.	*Eluting agent*	*Barium recovery % (50-ml fraction of effluent)*				*Total barium recovery %*	*Elution constant, E*	*Bed distribution coefficient $D = 1/E$*
		I	*II*	*III*	*IV*			
1	HNO_3, 1 *M*	...	...	...	...	4.6	—	—
	HNO_3, 1.5 *M*	2.5	3.7	17.8	56.1	80.1	0.1686	5.930
	HNO_3, 2 *M*	10.8	60.1	25.7	3.7	100.3	0.3727	2.683
	HNO_3, 3 *M*	32.9	62.4	4.2	1.4	100.9	0.5343	1.872
	HNO_3, 4 *M*	71.6	22.6	4.5	2.5	101.2	0.9439	1.060
2	HCl, 2 *M*	...	...	...	...	12.3	—	—
	HCl, 3 *M*	3.1	13.4	21.2	61.9	99.6	0.1954	5.119
	HCl, 4 *M*	4.0	15.9	65.8	15.5	101.2	0.2861	3.495
3	NH_4Cl, 2 *M*	...	...	...	...	9.4	—	—
	NH_4Cl, 3 *M*	1.9	2.2	35.2	62.9	102.2	0.1686	5.930
	NH_4Cl, 4 *M*	1.6	3.9	68.3	22.2	96.0	0.2322	4.306
4	$NaNO_3$, 1 *M*	...	...	...	...	10.5	—	—
	$NaNO_3$, 2 *M*	1.8	4.3	50.3	39.8	96.2	0.2322	4.306
	$NaNO_3$, 3 *M*	1.6	74.3	17.2	5.6	98.7	0.3727	2.683
5	NaCl, 2 *M*	...	...	...	...	10.7	—	—
	NaCl, 3 *M*	2.7	3.6	17.1	45.5	68.9	0.1686	5.930
	NaCl, 4 *M*	2.4	4.2	44.4	42.9	93.9	0.2322	4.396
6	CH_3COONH_4, 2 *M*	...	...	...	...	24.1	—	—
	CH_3COONH_4, 4 *M*	1.3	78.7	21.5	1.6	103.1	0.3727	2.683
7[a]	Citric acid 5% pH = 5.0	...	...	...	...	39.2	—	—
8[a]	Tartaric acid 5% pH = 6.8	...	...	...	...	9.1	—	—
9	EDTA, 0.01 *M* pH = 9.0	...	...	...	...	10.1	—	—

[a] Effluent collected up to 300 ml.

efficiency as: Tartaric acid < EDTA < citric acid < ammonium acetate < sodium chloride < ammonium chloride < hydrochloric acid < sodium nitrate < nitric acid. For routine work, however, hydrochloric acid (3–4 *M*) is appropriate owing to its ease of volatility in the assaying step. Ammonium chloride (3–4 *M*) may be used with the advantage that no evaporation is required and barium may be directly estimated.

Ion-exchange separations

These separations are feasible because of the difference in the exchange potential of a number of cations with respect to the resin. The cations may be arranged[14] qualitatively in order of decreasing selectivity of the Dowex 50W:

$$Ba^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2} > Be^{+2}$$
$$Ag^{+} > Tl^{+} > Cs^{+} > Rb^{+} > NH_4^{+} > K^{+} > Na^{+} > H^{+} > Li^{+}$$

1 *M* hydrochloric acid is an efficient eluant for cations such as uranium(VI), copper(II), mercury(II), caesium, zinc and cadmium but it is a poor eluant for barium. Hence it is possible to remove first the aforesaid cations with 1 *M* hydrochloric acid

and subsequently barium with 4 *M* hydrochloric acid. The effluent lot containing barium was evaporated to dryness and estimated as before. Attempts to separate aluminium were not successful since part of it was eluted along with barium giving high results. In case of the separation of silver from barium, nitric acid was substituted for hydrochloric acid as an eluant.

Barium does not form any complex[15] with citric acid at pH *ca.* 3.0 or with EDTA (disodium salt) at pH 2.0–3.0. Hence cerium(IV), zirconium(IV), iron(II), bismuth(III) and thorium complexes under these conditions can be easily separated from barium by passage through the cation exchange column. Cerium(IV) and zirconium(IV) were separated by complexing with 5% citric acid at pH 2.7 whereas the others were complexed with EDTA at pH 2.0–2.2. In both cases 4 *M* hydrochloric acid was the eluant; the effluent lot was evaporated completely to dryness and excess of citric acid or EDTA was destroyed by nitric–perchloric acid treatment before the estimation of barium.

TABLE II

ION-EXCHANGE SEPARATIONS OF BARIUM

Ba = 14.56 mg

No.	*Foreign ion*	*Added, mg*	*Barium found, mg*	*Total barium recovery %*
1	U(VI)	69.7	14.80	101.7
2	Cu(II)	30.0	14.25	97.9
3	Hg(II)	30.0	14.43	99.3
4	Cs	28.8	14.48	99.4
5	Zn	30.0	14.62	100.5
6	Cd	29.0	14.39	98.9
7	Al	29.0	16.28	111.8
8	Ag	14.0	14.56	100.0
9	Ce(IV)	29.0	15.11	103.8
10	Zr(IV)	20.9	14.21	97.7
11	Th	30.0	14.42	99.1
12	Bi(III)	29.0	14.46	99.4
13	Fe(III)	14.5	14.33	98.5

Separations from lead

The ion-exchange characteristics of lead on a Dowex-50 column have already been studied[3]. It is worthwhile to compare the separation factors for barium/lead on the basis of their bed distribution coefficients under comparable conditions. The common eluting agents, nitric acid (2–4 *M*), sodium nitrate (2 *M*) and ammonium acetate

TABLE III

SEPARATION FACTORS FOR BARIUM–LEAD BED DISTRIBUTION COEFFICIENT (*D*)

Eluant	*Bed distribution coefficient (D)*		*Separation factor*
	Barium	*Lead*	$= D_{Ba}/D_{Pb}$
HNO_3, 2 *M*	2.683	2.564	1.047
HNO_3, 3 *M*	1.872	1.443	1.297
HNO_3, 4 *M*	1.060	1.443	0.7345
$NaNO_3$, 2 *M*	4.306	3.684	1.169
CH_3COONH_4, 1 *M*	Very large	2.564	Very large
CH_3COONH_4, 4 *M*	2.683	1.443	1.860

(4 *M*) were used for these calculations. It follows from Table III that the best separation is obtained with 1 *M* ammonium acetate since the separation factor is very large. This has been actually confirmed[3].

The separations of barium from other important fission product elements such as cerium, zirconium, caesium, zinc, cadmium and silver and also from uranium and thorium attach unique significance to the technique of ion-exchange chromatography since such procedures are valuable in nuclear energy programmes. Again separations from common metals like copper, bismuth and iron are also of importance. The overall operations in this method take 3–4 h. The results are reproducible to ± 3%.

ACKNOWLEDGEMENTS

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SUMMARY

The cation-exchange behaviour of milligram amounts of barium on Dowex 50W-X8 has been studied. Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, sodium chloride, ammonium acetate, citric acid, tartaric acid and EDTA were tested as eluants. 200–300 ml of 3 *M* nitric acid, hydrochloric acid, sodium nitrate or ammonium chloride elute 30 mg of barium from a 1.4 × 20 cm bed. The relative efficiency of the eluants is discussed in terms of their elution constants and bed-distribution coefficients. Barium can be separated from a wide variety of metals.

RÉSUMÉ

Les auteurs ont effectué une étude du comportement du baryum sur une colonne échangeur de cations. Cet élément a ainsi pu être séparé de produits de fission importants tels que Cs, Zn, Cd, Ag, Ce(IV) et Zr, de même que des éléments suivants: U(VI), Th, Bi, Cu, Hg(II) et Fe(III).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das Verhalten von Barium gegenüber einem Kationen-Austauscherharz mit Angaben über Eluierungsmittel. Barium kann nach dieser Methode getrennt werden von: Cs, Zn, Cd, Ag, Ce(IV), Zr, U(VI), Th, Bi, Cu, Hg(II) und Fe(III).

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APPLICATIONS OF THE METAL PYRIDINE THIOCYANATE REACTION TO QUALITATIVE ANALYSIS

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Several divalent cations react with pyridine and thiocyanate to form water-insoluble compounds which are extracted with chloroform[1]. The chloroform extracts can be used for the spectrophotometric determination of the cations, *e.g.*, copper, nickel, cobalt, iron(II), manganese[2]. Observation of the chloroform extract can be used as a rapid qualitative test for certain cations. Furthermore, a solution of copper–pyridine complex can be used to test for certain anions that react in a manner similar to thiocyanate[3]. Some applications are given below.

Test for cations

Treat a few drops of sample solution with a drop of solution containing 8% pyridine and 3% potassium thiocyanate; add one or two drops of chloroform and shake or mix thoroughly. The color of the extract for various cations is shown in Table I, along with the approximate sensitivity of the test. The following cations, under the conditions of the test, either do not give a pyridine thiocyanate reaction, or give a colorless chloroform extract: silver, zinc, cadmium, mercury(I,II), lead, tin(II,IV), aluminum, chromium(III), titanium(IV) (TiO^{+2}), zirconium(IV) (ZrO^{+2}), platinum(IV), vanadyl (VO^{+2}), uranyl (UO_2^{+2}).

TABLE I

COLOR OF CHLOROFORM EXTRACT OF METAL PYRIDINE THIOCYANATES

Metal ion	*Color of extract*	*Sensitivity, mg/ml*
Copper	Chartreuse to emerald-green	0.1
Nickel	Sky-blue	2
Cobalt	Pink-red	1
Iron(II)	Lemon-yellow	0.1
Manganese(II)	Pale pink	10

The principal utility of the test is the speed with which a check can be made for an ion, for example, differentiating between Cu^{+2} and VO^{+2} when a blue solution, or between Ni^{+2} and Cr^{+3} when a green solution is obtained in the course of an analysis.

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It should be remarked that if thiocyanate is added before pyridine, rather than simultaneously or in the reverse order, vanadyl ion forms a blue-white precipitate giving a deep blue chloroform extract. By the same procedure, uranyl ion forms a yellow-orange chloroform extract. Addition of pyridine before or simultaneously with thiocyanate precipitates the hydrous oxides of vanadium and uranium.

Test for anions

The reagent is prepared by adding pyridine to 0.1 *M* copper sulfate solution until the blue color is not darkened by more pyridine. *Procedure*: To a few drops of sample solution add 1 or 2 drops of the copper–pyridine reagent and 1 or 2 drops of chloroform. Shake or stir thoroughly, let the chloroform settle, and observe. The colors produced by some common anions are shown in Table II. Chloride, fluoride, and perchlorate give a negative test.

TABLE II

COLOR OF COPPER PYRIDINE COMPOUNDS IN CHLOROFORM

Anion	*Color of extract*
Thiocyanate	Emerald-green
Cyanate	Yellow-green
Cyanide	Greenish-yellow
Peroxydisulfate	Yellow-green
Iodide	Brown
Bromide	Blue-green

Test for aliphatic tertiary amines and pyridine bases

Reagent: Add 10% potassium thiocyanate solution to 0.1 *M* copper sulfate solution until the blue color is discharged. Filter or allow the precipitate to settle, and use the filtrate or decanted solution.

Procedure: Add 2 or 3 drops of the copper thiocyanate reagent to a few drops of sample in a small test tube, or in the depression of a white spot plate. Formation of a green precipitate shows the presence of an aliphatic tertiary amine or a pyridine base. Primary amines give no precipitate; secondary amines give either a yellow precipitate, or none at all. As little as 0.001% pyridine in water can be detected.

SUMMARY

The reaction of pyridine with certain cations can be used as a quick means of detecting the latter, based upon the color of the chloroform extract of the metal pyridine thiocyanate. The copper–pyridine complex (*e.g.*, sulfate solution) can also be used as a reagent for the detection of several anions that give reactions similar to that of thiocyanate. A saturated solution of copper thiocyanate is a sensitive reagent for the detection of pyridine, and for differentiating tertiary amines from primary and secondary amines.

RÉSUMÉ

Plusieurs cations peuvent être identifiés par le réactif pyridine–thiocyanate de potassium, avec extraction dans le chloroforme. De même divers anions peuvent réagir (comme le thiocyanate) avec le complexe cuivre–pyridine. D'autre part, une solution de thiocyanate de cuivre peut être utilisée pour la détection de la pyridine et d'amines tertiaires.

ZUSAMMENFASSUNG

Die Reaktion einer Anzahl Kationen mit Pyridin–thiocyanat, die unter Bildung gefärbter, mit Chloroform extrahierbarer Verbindungen verläuft, kann zum schnellen Nachweis dieser Kationen verwendet werden. Mit einer Lösung von Kupfer–Pyridin können verschiedene Anionen, die ähnlich wie Thiocyanat reagieren, nachgewiesen werden. Kupferthiocyanat ist ein empfindliches Nachweisreagenz für Pyridin und tert. Amine.

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SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM WITH *sym*-DIPHENYLCARBAZONE*

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The classical method for the determination of rhodium involves its separation from all other heavy metals and final weighing as metal[1]. Other gravimetric methods using organic precipitants have been proposed. Watanabe[2] used 1-nitroso-2-naphthol, with subsequent ignition of the precipitate to the oxide. Haines and Ryan[3] precipitated rhodium with 2-mercaptobenzoxazole or 2-mercaptobenzothialoze, finally igniting to the metal. Duval *et al.*[4] recommended the 2-mercaptobenzoxazole precipitate as a weighing form, and the 2-mercaptobenzothiazole precipitate was used as the weighing form by Ubaldini[5]. Duval[4], and also Pshenitsyn[6], precipitated rhodium with thionalide and used the precipitate as the weighing form; Currah *et al.*[7] used the precipitate formed by reaction of rhodium with thiobarbituric acid.

A titrimetric determination using thionalide, described by Kienitz and Rombock[8], is subject to many interferences. Polarographic determination of rhodium has been made in solution as fluoride[9], cyanide or thiocyanate[10], or pyridine[11]. Rhodium can be determined spectrographically[12].

Spectrophotometric determination of rhodium has been made with hypochlorite[13], and with tin(II) in hydrochloric acid[14,15]. Ryan[16] proposed 2-mercapto-4,5-dimethylthiazole and 2-mercaptobenzoxazole as spectrophotometric reagents, and Watanabe[17] showed that the precipitate obtained with 1-nitroso-2-naphthol could be dissolved in acetone for spectrophotometric measurement.

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In the previous spectrophotometric methods the specific absorptivity ranges from about 0.04 to 0.11 per p.p.m.-cm, and the methods are subject to varying degrees of interference from the other platinum elements and gold, as well as from many anions. In the method presented here the specific absorptivity is about 0.60 per p.p.m.-cm, and the interferences from other platinum elements and gold are minimized by the pretreatment procedure before color development.

APPARATUS

Absorbance measurements were made with a Beckman Model DU quartz spectrophotometer. Scans of absorbance curves over a range of wave lengths were made with a Beckman Model DK-1 recording spectrophotometer. Matched cells of 1.00-cm optical path were used. Measurements of pH were made with a Beckman Zeromatic pH meter, using glass and calomel electrodes. A Mettler Model M5 micro balance was used for weighings made for standardization of the rhodium solution. Calibrated flasks and pipets were used. For fuming down solutions with perchloric acid, a 125-ml Erlenmeyer flask was rounded on the bottom, leaving just enough flat surface to allow the flask to stand. This shape allowed the fuming to proceed almost to dryness without baking the solids on the bottom.

REAGENTS

Standard rhodium solution: The solution was prepared from C.P. rhodium(III) chloride tetrahydrate (A. D. Mackay, Inc.) and was standardized by reduction to and weighing as metal, by the following procedure: 25.00-ml aliquots of the rhodium chloride solution were treated with ten times the calculated amount of magnesium turnings. Hydrochloric acid was added from time to time to keep magnesium hydroxide dissolved. After about 48 h the samples were heated with more hydrochloric acid to dissolve all the magnesium. The precipitated rhodium metal was filtered on medium porosity ashless filter paper and washed with 0.1 *N* hydrochloric acid until free from magnesium as shown by negative test with titan yellow. Washing was completed with water, to remove hydrochloric acid. The paper containing the precipitate was placed in a porcelain boat (previously ignited to constant weight in hydrogen), was dried 2 h at 120°, and was then ignited in a muffle furnace to about 1000°. The precipitate was finally ignited to constant weight in hydrogen. Triplicate 25.00-ml aliquots of stock solution gave the following weights of rhodium metal: 0.10639 g, 0.10630 g, and 0.10612 g; average, 0.10627 g. The calculated concentration of the rhodium stock solution was 0.04131 *M*, or 4251 p.p.m.

Color reagent: sym-Diphenylcarbazone, $C_6H_5\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH\cdot C_6H_5$–$C_6H_5\cdot N{:}N\cdot CO\cdot NH\cdot NH\cdot C_6H_5$ (Eastman No. 4459) was obtained from Distillation Products Industries. A 0.025 *M* solution in acetone was used as the color-developing reagent. Slight variations in absorbance resulting from the use of different preparations of the reagent solution were eliminated by the addition of a small amount of acetic acid (1 ml of glacial acetic acid per liter of acetone used as solvent).

Buffer: A 0.100 *M* solution of monochloroacetic acid was partially neutralized with sodium hydroxide to give a solution of pH 3.0. The solution was also made 0.10 *M* in sodium perchlorate to provide a constant ionic strength.

Perchloric acid: A 0.10 *M* solution was partially neutralized with sodium hydroxide to give a solution of pH 3.0.

Other reagents: Substances used for testing interferences were reagent quality chemicals. Chlorides of iron, cobalt, nickel, and ruthenium, nitrates of copper, silver, lead, manganese, and chromium, and oxides of mercury and zinc were used as sources of the respective metal ions. Pure metals gold, platinum, and palladium were dissolved in aqua regia, then evaporated repeatedly with hydrochloric acid. Iridium metal was fused with sodium peroxide, then converted to chloride. Osmium solution was made by dissolving osmium tetroxide in sodium hydroxide solution. Other reagents included sodium hydroxide, monochloroacetic acid, sodium perchlorate, methanol, and N,N-dimethylformamide.

DEVELOPMENT OF THE METHOD

Sixty-seven organic compounds, which might be expected to coordinate with rhodium, were tested for possible use as color-developing reagents. Rhodium was used in solutions of the chloride, bromide, iodide, thiocyanate, and perchlorate. Reaction media used included aqueous solutions of pH 1, 2, 3, and 4, glacial acetic acid, ethanol, acetone, and pyridine. Quantities were adjusted so that the rhodium concentration was approximately 5 p.p.m. Any immediate reaction was noted, then each sample was heated to boiling and again examined. About half of the reagents formed a yellow solution or precipitate. A few of the compounds gave color changes due to reagent only, *i.e.*, the same color change whether rhodium was present or not. About one-third of the compounds tested gave no visible evidence of reaction. Thiodiphenylamine, 5-*p*-dimethylaminobenzilidenerhodanine, diphenylthiocarbazone, quinoxaline-2,3-dithiol, and *sym*-diphenylcarbazone gave colors sufficiently intense to warrant further testing. *sym*-Diphenylcarbazone was chosen for study because it gave a very intense purple color which appeared to be proportional to the rhodium concentration.

Review of the literature showed that *sym*-diphenylcarbazone and/or diphenylcarbazide have been used for the detection or determination of a large number of substances. The carbazide[18] has been used for the detection of cadmium, chlorate, chloride, chromium, copper, hydrogen peroxide, iron, magnesium, mercury, molybdenum and periodate, and for the determination of arsenic, chloride, chromium, iron, lead, mercury, molybdenum, phosphorus, sulfate and vanadium, and for the micro determination of copper[19]. The carbazone has been used to detect cadmium, chromium, copper, iron, mercury and molybdenum, and to determine lead, mercury and zinc[18]. These reagents have not been used for rhodium or the other platinum elements; in fact, in a procedure for a confirmatory test for mercury[18], rhodium, platinum and iridium were stated not to interfere under the conditions of the test.

STANDARD PROCEDURE

Treat the sample (standard solution, or unknown solution for analysis) with about 10 ml of 70–72% perchloric acid, and fume down to 1 or 2 ml to remove any halides and/or nitrate that may be present from preparation of the sample. Add water to

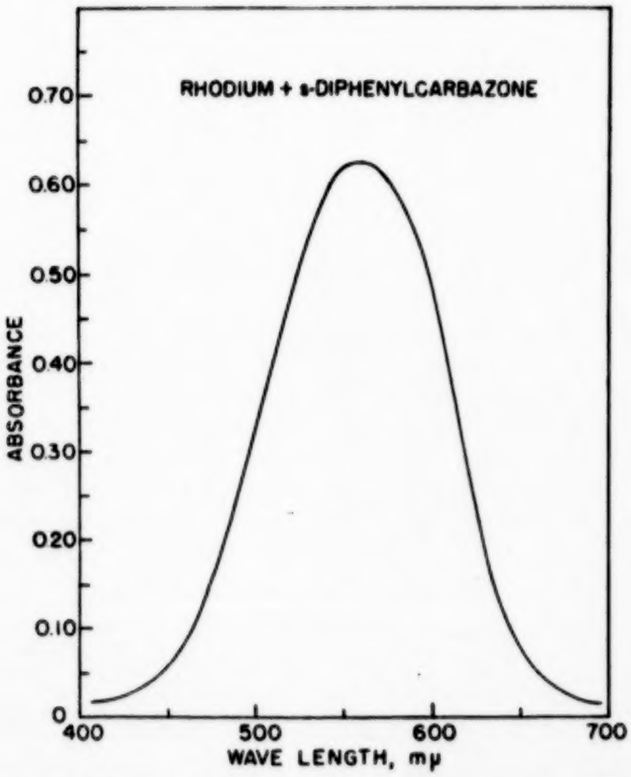

Fig. 1. Spectral curve for rhodium with *sym*-diphenylcarbazone. Rhodium concentration 1.066 p.p.m.

about 80–90% of the final volume, adjust to pH 3.0 (use pH-meter), then dilute to the mark in a volumetric flask.

Pipet 5 ml of monochloroacetic acid buffer into a 50-ml Erlenmeyer flask; add perchloric acid (of pH 3.0) in such volume that sample plus perchloric acid is 10.0 ml. Add the sample solution (no more than 10.0 ml) and 1.0 ml of *sym*-diphenylcarbazone reagent; wash down the walls of the flask with acetone. Place the flask in a boiling water bath for 30 min. Cool, and transfer the contents to a 50-ml volumetric flask; rinse 2 or 3 times with methanol. Wash down the reaction flask with 5 ml of N,N-dimethylformamide; tilt the flask and rotate it so as to wet the walls with the solvent. Transfer the rinsings to the volumetric flask, and again rinse with small portions of methanol. Cool the mixture to room temperature, dilute with methanol to the mark, and measure the absorbance at 565 mμ against a reagent blank prepared in the same way as the sample solution.

TABLE I

DATA FOR CALIBRATION CURVE

Rhodium conc. p.p.m.	*Absorbance at 565 mμ*	*Absorptivity per p.p.m. cm*
0.107	0.063	0.589
0.212	0.129	0.609
0.424	0.255	0.601
0.638	0.386	0.605
0.851	0.511	0.600
1.066	0.636	0.597
1.278	0.751	0.588
1.429	0.875	0.612
1.699	0.999	0.588
2.124	1.280	0.602
	Average:	0.599
	Standard Deviation:	0.009

The absorbance spectrum of the rhodium complex, for 1.066 p.p.m. of rhodium, is shown in Fig. 1. The data shown in Table I were used to construct the calibration graph; each absorbance value given in the table is the average of 6 separate preparations in which the average relative deviation in absorbance was 0.5%. The system conforms to Beer's law. The optimum concentration range for measurement at 1-cm optical path is about 0.3 to 1.5 p.p.m.[20]. The molar absorptivity of rhodium in the complex is $6.17 \cdot 10^4$ l mole^{-1}cm^{-1}.

Reproducibility

In a test of the precision of the method, 33 samples each containing 0.851 p.p.m. of rhodium (about the center of the optimum concentration range) were prepared by the standard procedure. The absorbance ranged from 0.497 to 0.519; the average was 0.511, and the standard deviation was 0.005 or about 1%.

EFFECT OF VARIABLES

Effect of pH

A series of nine buffer solutions was made; 0.100 *M* chloroacetic acid was adjusted to the desired pH by adding sodium hydroxide. Nine solutions of perchloric acid were also prepared, one corresponding to each buffer solution, by partial neutralization of 0.10 *M* perchloric acid with sodium hydroxide. The procedure followed for color development was otherwise the same as in the standard procedure; in each case the rhodium concentration was 0.851 p.p.m. The color of the reaction system changed from purple to red as the pH increased. The data of Table II show that the pH is quite critical, and must be controlled at 2.9–3.0 in order to obtain maximum sensitivity and reproducibility. Because of the close control required, it is necessary to adjust the sample and the perchloric acid diluent to pH 3.0.

Effect of amount of reagent

Samples were made according to the standard procedure, at a rhodium concentration of 0.851 p.p.m., except that the volume of reagent solution was varied from 0.7 to 1.2 ml. The absorbance was measured against a blank containing 1.0 ml of reagent solution. The blank was then read against pure methanol, and the absorbances of the sample solutions were corrected accordingly. The data of Table III show that the amount of reagent solution used is not highly critical.

TABLE II

EFFECT OF pH

pH	*Absorbance at 565 mμ*
1.5	0.106
2.0	0.317
2.5	0.456
3.0	0.508
3.5	0.420
4.0	0.357
4.5	0.320
5.0	0.283
6.0	0.370

Effect of amount of buffer

Solutions were made containing 0.851 p.p.m. of rhodium and volumes of buffer varying from 3.0 to 7.0 ml; in each solution the total water content was 15.0 ml. The absorbance of the solutions was 0.515 ± 0.003, showing that the amount of buffer solution used is not critical.

TABLE III

EFFECT OF VARYING AMOUNT OF REAGENT

ml of reagent	*Absorbance at 565 mμ*
0.7	0.484
0.8	0.496
0.9	0.507
1.0	0.515
1.1	0.521
1.2	0.521

TABLE IV

EFFECT OF VARYING TOTAL WATER CONTENT

Total water ml	*Absorbance at 565 mμ*
12.0	0.530
13.0	0.528
14.0	0.520
15.0	0.514
16.0	0.508
17.0	0.503
18.0	0.500

Effect of amount of water

Solutions made according to the standard procedure contain 15.0 ml of water, consisting of the sum of the buffer solution, the sample solution, and the perchloric acid solution. For testing the effect of this factor, the water content was varied from 12.0 to 18.0 ml, while keeping all other factors the same as in the standard procedure. Table IV shows the absorbances of the solutions, which contained 0.851 p.p.m. of rhodium. The data indicate that the total water content must be kept constant in order to obtain reproducible results.

Effect of time of heating

Solutions were prepared according to the standard procedure, except that the time of heating in the boiling water bath was varied from 15 to 45 minutes. The absorbance, for a given amount of rhodium, increased gradually with the period of heating, up to 30 minutes, after which it was constant within the limits of experimental error.

Effect of order of addition of components

Solutions were made in accordance with the standard procedure, except that the order of addition of the components was varied. In only one case was there any effect; when the order of addition was sample, reagent, perchloric acid, and buffer, the absorbance was low.

INTERFERENCES

In the evaluation of the precision of the method, using 0.851 p.p.m. of rhodium, the range of absorbances was about ±0.01 absorbance unit from the average value obtained from 33 samples. A foreign substance will be considered interfering if the absorbance of a solution containing 0.851 p.p.m. of rhodium and the foreign substance has an absorbance 0.02 unit lower or higher than the (average) value for rhodium alone, *i.e.*, an absorbance below 0.49 or above 0.53. The tolerance for a foreign ion is

TABLE V

TOLERANCE FOR FOREIGN IONS

Foreign ion	*Tolerance conc., p.p.m.*
Palladium(II)	1.5
Platinum(IV)	10[a]
Iridium(IV)	5[b]
Gold(III)	10[a]
Iron(III)	9
Cobalt(II)	2
Nickel(II)	0.5
Manganese(II)	N.D.[c]
Silver(I)	12
Copper(II)	0
Zinc(II)	4
Lead(II)	5
Chromium(III, VI)	Nil[d]
Mercury(II)	Nil[d]

[a] This is the concentration before fuming with perchloric acid, which removes the platinum or gold by precipitation.

[b] Present as iridium(IV) chloride; see comments in text.

[c] Exact tolerance not determined; completely precipitated by fuming down with perchloric acid.

[d] Tolerance in final solution; see comments in text.

the maximum amount of the substance that can be present without exceeding these limits. The compounds used as sources of foreign ions are given earlier under "*Reagents*".

Interference was evaluated by adding the foreign ion solution to the rhodium perchlorate solution, and fuming down with perchloric acid almost to dryness; the sample was then adjusted to pH 3.0 and the color was developed by the standard procedure. Tolerances are shown in Table V, and certain cases are discussed briefly below.

Manganese is precipitated as the hydrous dioxide by fuming down with perchloric acid; platinum and gold are also completely precipitated, probably as hydrous oxides. However, the precipitates carry down some rhodium, the effect increasing with time of fuming. A sample originally containing platinum or gold must be developed and measured within 1 or 2 h after fuming in order to avoid loss of rhodium.

Although iridium reacts with *sym*-diphenylcarbazone to form a purple solution having maximum absorption at the same wave length (565 mμ) as the rhodium solution, it also interferes with the rhodium analysis due to the low pH (about 2.5) at which iridium hydrous oxide precipitates from perchlorate solution; rhodium is extensively coprecipitated.

Osmium and ruthenium can be tolerated in relatively large amounts in the original solution, because they are removed as their volatile tetroxides during the fuming with perchloric acid[21].

sym-Diphenylcarbazone has long been used as a colorimetric reagent for chromium[22] and for mercury[23], and as an indicator in mercurimetric titrations[24]. During the fuming with perchloric acid in the interference test, some chromyl chloride vapor was observed. Well-known methods exist for the removal of chromium by volatilization as chromyl chloride[25], and for the removal of mercury by volatilization of mercury(II) chloride[26].

Copper(II) reacts with *sym*-diphenylcarbazone to form a bulky, red-pink precipitate difficultly soluble by the procedure used for rhodium. Owing to the strong catalytic effect of copper on the auto-oxidation of the reagent[27], the precipitate and the dissolved copper compound are completely destroyed, giving a colorless solution after standing about 3 h at room temperature. In the presence of copper, the rhodium color is destroyed much more slowly; nevertheless, by the time the copper color is gone, enough rhodium color has also been destroyed to make the rhodium results low.

Because sulfate is not removed by fuming with perchloric acid, the sample should be prepared for analysis without using sulfate (sulfuric acid). Sulfate, if present in the color-developed sample, results in a lowered absorbance; the exact tolerance was not determined.

DISCUSSION

The purple color obtained with rhodium was first observed by the use of an alcoholic solution of a discolored sample of 1,5-diphenylcarbohydrazide (diphenylcarbazide). KRUMHOLZ AND KRUMHOLZ[28] state that an alcoholic solution of either diphenylcarbazide or diphenylcarbazone converts to a 1 : 1 mixture of the two substances, due to air oxidation of the carbazide or auto-oxidation of the carbazone. Therefore, there is uncertainty as to whether it is the carbazide or the carbazone that reacts with the rhodium. An effort to decide between the alternatives was made by using acetone solutions of the pure carbazide and the pure carbazone prepared according to the method of KRUMHOLZ AND KRUMHOLZ[28]. When using either pure compound, the absorbance produced by a given amount of rhodium was less than when a 1 : 1 mixture of the compounds was used. Therefore, the commercially available *sym*-diphenylcarbazone was used as the reagent. This substance is represented on the label as a 1 : 1 molar mixture of diphenylcarbazide and diphenylcarbazone; the manufacturer[29] bases this composition on the work of KRUMHOLZ AND KRUMHOLZ.

The extreme water-insolubility of the reagent and of the purple rhodium product was the source of much trouble in the development of the method. Three different approaches were tried: (*1*) nonaqueous medium, except for the small amount of water left after fuming down the sample with perchloric acid; (*2*) use of water and organic solvents miscible with it, during formation of the product; (*3*) aqueous medium for formation of the product, followed by dissolution of the precipitate in organic solvents.

The rhodium perchlorate residue remaining after fuming the sample with perchloric acid was insoluble in benzene and in chloroform, but was readily soluble in methanol, ethanol, 2-propanol, 2-methyl-2-propanol, 2-methyl-2-butanol, *p*-dioxane, ethyl acetate and amyl acetate. In these organic media the reaction of rhodium with *sym*-diphenylcarbazone is more rapid than in aqueous medium.

Buffer systems for the nonaqueous media were made by dissolving an organic acid in the solvent being tested, and neutralizing with alcoholic sodium methoxide to the desired "pH" as indicated by a pH meter. The acids used in preparing the buffers were formic, acetic, benzoic, monochloroacetic, citric, tartaric, and mixtures of mono- and trichloroacetic. The optimum "pH" was 5 for color development in the nonaqueous media.

Methanol was found to be the most suitable solvent for all components of the color-forming reaction. However, in methanol and other organic liquids the absorbance was poorly reproducible. Furthermore, solutions of rhodium perchlorate in methanol showed an aging effect, due apparently to reduction of rhodium(III) to a lower oxidation state. There was no evidence of reduction of rhodium to the metal, even by prolonged boiling, if a chloroacetate buffer was present, but the rhodium "found" by reaction with *sym*-diphenylcarbazone decreased on aging of the rhodium solution.

In the absence of any organic solvent, the purple rhodium precipitate adhered tenaciously to the walls of the reaction flasks. Although the precipitate is very soluble in ethyl acetate and amyl acetate, in the presence of the aqueous phase these solvents failed to dissolve completely the colored precipitate adhering to the flask, and nonreproducible absorbances resulted. The use of acetic acid and concentrated buffer eliminated the solubility problem, but nonreproducible absorbances were still obtained, probably due to some reduction of the rhodium(III) by the hot organic solvent.

Because all efforts to form and dissolve the purple rhodium product in the same vessel were unsuccessful, it was decided to transfer the aqueous mixture to a volumetric flask, then to attack the material adhering to the reaction flask with powerful solvents such as methanol and N,N-dimethylformamide without the interfering effect of water. This procedure was successful and resulted in the standard procedure described earlier.

When diphenylcarbazide or diphenylcarbazone reacts with a metal ion, the question of what organic species is involved is difficult to answer. The carbazide is very easily air oxidized to the carbazone, which in turn is easily air oxidized to the carbodiazone.

In addition, the carbazone undergoes an intramolecular oxidation–reduction reaction which is catalyzed by certain metal ions, most notably copper[27]. Both the carbazide and the carbazone can exist in either keto or enol forms; the keto form of both compounds gives the more intensely colored reaction products[18].

FEIGL AND LEDERER[30] state that diphenylcarbazide is a specific reagent for elements of periodic group two, and that the products are carbazides, not carbazones, in which metal substitution occurs on the 2-nitrogen atom. KRUMHOLZ AND KRUMHOLZ[28] report that chromate gives a pale rose color with pure diphenylcarbazone, in contrast to the intense violet color produced by a mixture of diphenylcarbazide and diphenylcarbazone. KRUMHOLZ AND HÖNEL[31] state that diphenylcarbazide is a better reagent than diphenylcarbazone for chromium. BOSE[32] found that chromate oxidized the carbazide to the carbazone, and that the violet product was a chromium(II)-carbazone salt; he also found that chromate will oxidize the carbazone to carbodiazone, with the same chromium(II)-carbazone salt as the product. WELCHER[18] states than "in many tests involving diphenylcarbazide . . . diphenylcarbazone is present as an oxidation product."

The chemistry of the rhodium reaction is not clear. As stated earlier, the reaction between rhodium and pure diphenylcarbazone or pure diphenylcarbazide produces a less intense color than the 1 : 1 molar mixture of the two; in this respect the rhodium reaction is similar to that of chromium[28]. The possibility that the purple product is merely an oxidation product of the reagent was ruled out because treatment with various oxidizing agents — tin(IV), hydrogen peroxide, iodine, nitric acid, sodium bismuthate — produced only a yellow solution. In addition, attempts to reduce the purple rhodium solution with sodium bisulfite, hydrazine sulfate, and oxalic acid were unsuccessful.

The purple reaction product is uncharged, as shown by its failure to be retained on either an anion- or a cation-exchange resin.

The method of continuous variations[33] applied to the reaction system gave maximum absorbance at a reagent-to-rhodium ratio of 2 : 1; however, the curve of absorbance *vs.* mole fraction of reagent was considerably rounded near its maximum. The curves obtained by the method of mole ratios[34] were poorly defined as to any "breaks", and gave no useful information concerning the composition of the product. Because the reagent itself is a 1 : 1 molar mixture of diphenylcarbazone and diphenylcarbazide, the 2 : 1 reaction ratio of reagent to rhodium sheds little light on the actual reaction.

The great color stability of the rhodium complex, its uncharged nature, its extreme insolubility in water but solubility in organic solvents, and its intense color indicate a chelate structure, but the exact structure and the particular ligand species involved remain uncertain.

ACKNOWLEDGEMENT

The assistance provided by a grant from National Science Foundation (NSF Grant 1889) and by a grant from The University of Texas Research Institute (URI Project No. 637) to GILBERT H. AYRES, and a fellowship from Procter and Gamble Company to FRED L. JOHNSON, JR., are gratefully acknowledged.

SUMMARY

A sensitive spectrophotometric method for the determination of rhodium is based upon the purple color (absorbance maximum at 565 $m\mu$) produced by *sym*-diphenylcarbazone at pH 3.0; methanol and N,N-dimethylformamide are used as solvents. For measurement in a 1-cm cell, the optimum range is about 0.3 to 1.5 p.p.m., and the useful lower limit is about 0.05 p.p.m. Although careful regulation of pH is required, the other variables are not critical. Preparation of the sample requires fuming down nearly to dryness with perchloric acid; by this procedure chloride and nitrate are removed, osmium and ruthenium are completely volatilized as tetroxides, and platinum and gold are completely precipitated. Iridium, which forms a purple product with the reagent, also interferes on account of the low pH at which it precipitates as hydrous oxide. Interference from chromium(VI) and mercury(II) can be removed by volatilizing chromyl chloride and mercury(II) chloride, respectively. Copper(II) must be absent. The purple rhodium product is not retained on either cation- or anion-exchange resins. The method of continuous variations indicates a reaction ratio of 2 moles of *sym*-diphenylcarbazone to 1 mole of rhodium.

RÉSUMÉ

Une méthode spectrophotométrique sensible est proposée pour le dosage du rhodium. Elle est basée sur la coloration pourpre, obtenue au pH 3, avec la diphénylcarbazone. L'échantillon est attaqué par l'acide perchlorique, ce qui permet de chasser chlorures et nitrates, de volatiliser osmium et ruthénium (sous forme de tétroxydes) et de précipiter or et platine.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Rhodium. Sie beruht auf der Bildung einer Purpurfärbung mit Diphenylcarbazon bei pH 3. Durch Abrauchen mit Perchlorsäure werden Chloride und Nitrate entfernt, Osmium und Ruthenium als Tetroxyde verflüchtigt und Platin und Gold gefällt. Weitere Störelemente werden erwähnt.

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Anal. Chim. Acta, 23 (1960) 448–457

DETERMINATION OF SODIUM BY ATOMIC ABSORPTION SPECTROSCOPY

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The analytical application of the phenomenon of atomic absorption was first proposed by WALSH[1]. The principle of this procedure is that the sample is introduced into a flame (as in flame photometry). Light from a hollow cathode is then passed through the flame. The quantity of light absorbed at a selected wavelength is measured and the analysis of the sample determined.

There are numerous methods available for the determination of sodium. However, flame photometry is by far the most popular and has found widespread application. Numerous papers have been written describing rapid and accurate procedures for this determination. However, it is well known that under certain conditions this procedure produces inaccurate and imprecise results. This is particularly so if substantial quantities of other alkali metals are present in the sample. This can be a severely limiting factor under some conditions, *e.g.*, analysis of alkali salts for sodium content.

In the procedure described below, it was found that interference by other alkali metals is overcome. This allows the determination of sodium to be carried out accurately under most conditions and provides a universal procedure for the determination of that metal.

DISCUSSION

It has been observed and reported that the presence of excessive amounts of other alkali metals interferes with the flame photometric determination of sodium. Experience with atomic absorption spectroscopy has shown that it has a high degree of freedom from interference. Experiments were therefore carried out to test its application to the analysis of sodium in the presence of lithium and/or potassium.

It was shown that sodium atoms strongly absorb light of wavelength 5890 Å (D line). However, sodium in a flame also emits this wavelength very strongly. If we use a simple system involving a hollow cathode, a flame atomizer, a monochromator, and detector, we have the set-up as given in Fig. 1.

Confining our measurements to the 5890 Å line, the sodium lamp emits a signal of strength I_0. This is transmitted through the flame and is reduced to I_1 by atomic absorption by the sodium atoms. This light then passes through the monochromator to the detector which measures I_0 (no sample) and I_1. However, unfortunately the sodium in the flame also emits a signal strength E at this same wavelength. The detector, therefore, reads $I_1 + E$ instead of I_1. Since E is the emitted signal from the flame, it is subject to the same interferences as simple flame photometry.

MALMSTADT[2] illustrated the successful use of a null-point instrument for atomic absorption spectroscopy, in general, using sodium to demonstrate his findings. His equipment did not eliminate flame emission and as might be anticipated he experienced interference from potassium. However, this difficulty can be overcome by modulating the hollow cathode with a light chopper, and tuning the detector to the same frequency. This was found to be so experimentally, and the instrument measured only I_0 and I_1. Using the simple absorption formula $I_1 = I_0 e^{-KCl}$ (K = absorption coefficient, C = sodium concentration and l = path length), the sodium content of the flame and therefore of the aspirated sample can be obtained.

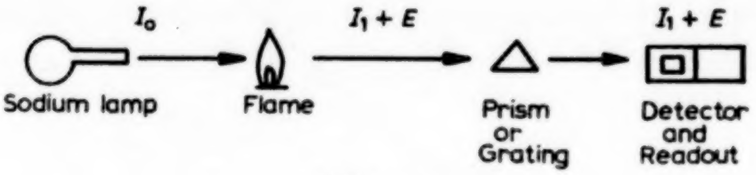

Fig. 1.

RESULTS

Using the principle outlined above, calibration curves over the range 0–1000 p.p.m. Na were obtained. These were plotted using the Ringbom relationship $K(1 - I_1/I_0) = \log C$. Assuming I_0 is constant, this can be reduced to $\log C = K'(I_0 - I_1)$. In this case $K = K'I_0$. As shown in Figs. 2 and 3, the most satisfactory working range under the conditions used was between 10–200 p.p.m. Na but it is clear from the data that the ranges 0–10 p.p.m. and 200–1000 p.p.m. Na can be utilized. The lower range can be expanded by using more sensitive conditions than those employed for this work. The data also indicated that the absorption coefficient varies with the sodium concentration. This means that calibration curves must be used to obtain accurate results. Precision data are given in Table I.

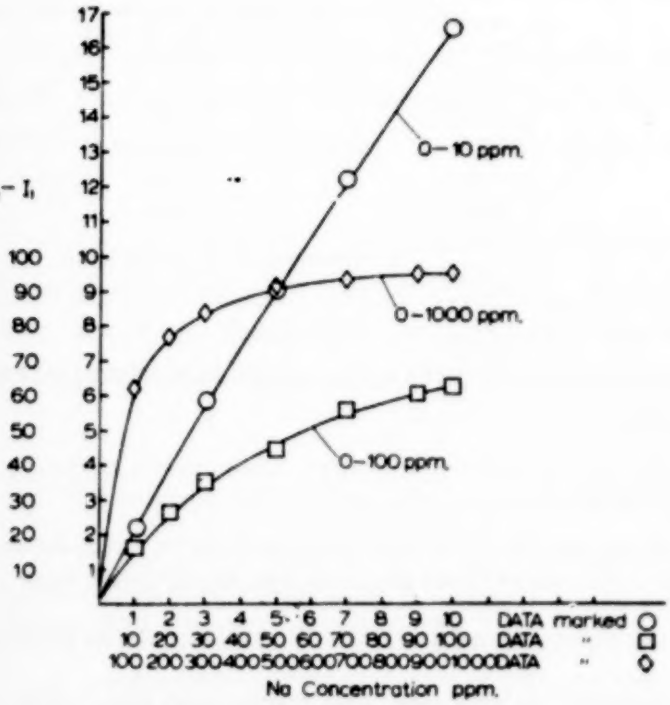

Fig. 2. Calibration data, $I_0 - I_1$ *vs.* concentration of Na in p.p.m. Scale $I_0 - I_1$ for range 0–10 p.p.m. Na was 0 to 17. Scale $I_0 - I_1$ for range 0–100 and 0–1000 p.p.m. Na was 0 to 100.

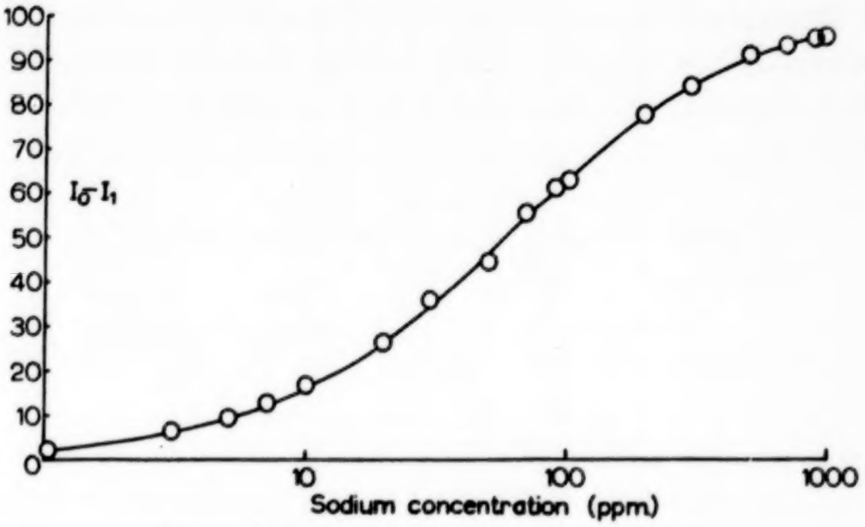

Fig. 3. Ringbom plot. Sodium *vs.* $I_0 - I_1$.

TABLE I

PRECISION DATA

Sodium concentration (p.p.m.)	*Precision 2σ (95% confidence) (p.p.m.)*	*No. of determinations*
5	0.14	$n = 11$
30	0.34	$n = 9$
200	0.28	$n = 10$

These results indicate that the precision of the procedure is within the noise level of the signal since in each case the variance in signal was less than half a division.

The interference of potassium or lithium was determined as follows:

TABLE II

Na present (p.p.m.)	*K present (p.p.m.)*	*Li present (p.p.m.)*	*Na found (p.p.m.)*	*Corrected for contaminations in Li and K salt (p.p.m.)*
10	5,000		12	10
500	5,000		500	500
10		5,000	12	10
500		5,000	500	500
Zero	5,000		2	Na content of K or Li salt
Zero		5,000	2	

Studies at lower potassium or lithium contents were not made, since it was apparent that no interference would be encountered.

EXPERIMENTAL

A schematic diagram of the equipment used is shown in Fig. 1 except that the hollow cathode and the detector were modulated and tuned together. The individual parts of the equipment were as follows:

Source, sodium vapor lamp: This source is not as stable as desirable, but can be used in conjunction with standards.

Burner: A Beckman flame atomizer burner was used in all cases. The flame used was a simple oxy–hydrogen flame.

Monochromator, detector and readout system: A modified Perkin-Elmer Model 13 spectrophotometer was used for this work. The pertinent modifications are shown in Fig. 4. This instrument was used for research in this project. A much simpler instrument embodying these modifications would no doubt work as successfully.

PROCEDURE

Standard solutions of sodium are prepared to cover the ranges 0–1000 p.p.m. If required, higher concentrations may also be prepared, but since this is an absorption procedure it becomes increasingly difficult to measure significant changes in the signal with concentration changes. The standards should be similar to the sample solutions to be run. As in flame photometry, the signal is affected by the predominant anion (chloride or sulphate) and the aspiration rate; this, in turn, is dependent on the viscosity, density, etc., of the aqueous solvent.

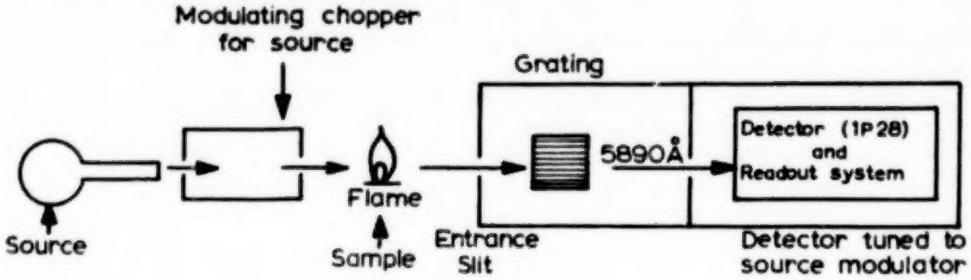
Modulating chopper for source
Grating
Detector (1P28) and Readout system
5890Å
Flame
Source
Sample
Entrance Slit
Detector tuned to source modulator

Fig. 4.

It was found experimentally that for most satisfactory results, the beam from the hollow cathode should traverse the flame at its widest point. Below this level in the flame, noise level increases and sensitivity decreases. It was also found that if organic solvents were used, care should be taken to traverse the flame at a point where combustion of the solvent is complete. This point must be determined experimentally for each type of solvent. Also, since it varies for different feed rates, it should be redetermined if a change in feed rate occurs.

After calibration, the samples may be run. If a hollow cathode is used as the source, the light beam will remain steady, but if a sodium lamp is used, some variation may be encountered. This difficulty can be overcome by running a standard and a sample within a short interval of time.

Results are calculated from the value of I_1 obtained, and the calibration curves used. Correction for the blank is made by calculating the blank in terms of p.p.m. sodium and subtracting this value from the apparent concentration of sodium in solution.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. W. L. Senn for his assistance in setting up the procedure, and Esso Standard, Division of Humble Oil and Refining Company, for permission to publish this work.

SUMMARY

A procedure has been developed for the determination of sodium by atomic absorption spectroscopy. The method eliminates interference from even large amounts of potassium and lithium.

RÉSUMÉ

Une méthode spectroscopique d'absorption atomique est proposée pour le dosage du sodium, en présence de potassium et de lithium.

ZUSAMMENFASSUNG

Beschreibung einer atomare absorptions-spektroskopischen Methode zur Bestimmung von Natrium neben Kalium und Lithium.

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SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM

o-PHENYLENEDIAMINE AS A REAGENT

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o-Phenylenediamine is used in the detection of nickel and vanadium and in the differentiation of ozone from hydrogen peroxide and nitrous acid[1]. On a study of the further use of this reagent it has been found by the author that it can also be used as a reagent for spectrophotometric determination of platinum(IV). The reagent at a pH range of 3–4 reacts with platinum(IV) in the cold to form an orange-colored complex having absorption maximum at 450 mμ. The color complex adheres to Beer's law for platinum concentration of 1 to 12 p.p.m., the optimum concentration range[2] being 4 to 12 p.p.m. where the per cent relative error per 1% absolute photometric error[3] is 2.87. The color reaction has a sensitivity of 1 part of platinum(IV) in 59,000,000 parts of the solution.

Application of "continuous variation"[4] and "molar ratio"[5] methods indicate that platinum(IV) combines with the reagent to form a 1 : 2 complex which has an average dissociation constant of $2.3 \cdot 10^{-8}$ at 10°.

EXPERIMENTAL

Apparatus

Wave length-transmittance curves of the color complex were obtained with a Beckman DK1 recording spectrophotometer and absorbance measurements of other solutions were made with a Beckman DU spectrophotometer. In all cases, 1.00-cm silica cells were used.

Hydrogen ion concentrations were measured with a Beckman model G pH meter.

Reagents

Standard platinum(IV) solution. For the preparation of a standard platinum(IV) solution an accurately weighed amount of pure platinum wire was dissolved in aqua regia, evaporated almost to dryness, taken up with 20 ml of 1 : 1 hydrochloric acid, and again evaporated to syrupy consistency. To remove all nitric acid and to destroy any nitrosoplatinic acid the above hydrochloric acid treatment was repeated three times. The material, after final evaporation, was transferred to a 250-ml volumetric flask by washing with water containing 2.5 ml of concentrated hydrochloric acid and diluted to volume. The strength of this solution was $5.3 \cdot 10^{-3}$ *M*. All other solutions were obtained by diluting this stock solution.

Reagent solution. A 1% solution of the reagent was obtained by dissolving 1.0 g of recrystallized *o*-phenylenediamine (m.p. 102°) in 100 ml water containing a little acetic acid.

Buffer solution. Buffer solutions of pH range 3.42–5.89 were obtained by mixing 0.2 *N* sodium acetate with 0.2 *N* acetic acid in varying quantities[6].

Other reagents. Solutions of other platinum metals and common ions were prepared in an identical way as described in a previous paper[7].

Experimental studies

Recommended procedure and spectral curves

Five ml of 1% reagent solution were added to the platinum(IV) solution taken in a 25-ml flask. The volume was then made up with the buffer of pH 3.42 and after allowing to stand for 25 min the absorbance was measured against a reagent blank. The spectral curves of the complex as shown in Fig. 1 indicate that maximum absorption (*i.e.* minimum transmittance) takes place at 450 mμ.

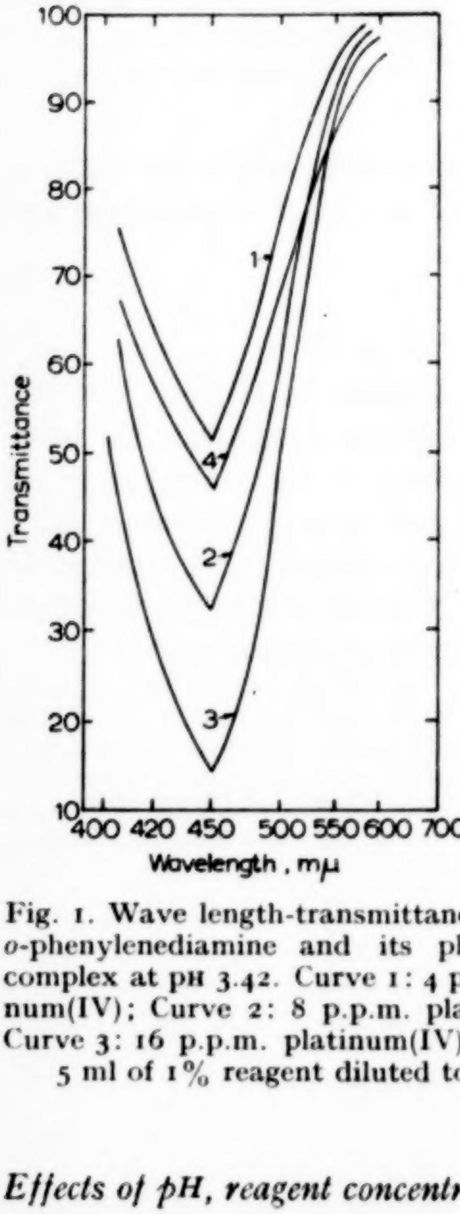

Fig. 1. Wave length-transmittance curves of *o*-phenylenediamine and its platinum(IV) complex at pH 3.42. Curve 1: 4 p.p.m. platinum(IV); Curve 2: 8 p.p.m. platinum(IV); Curve 3: 16 p.p.m. platinum(IV); Curve 4: 5 ml of 1% reagent diluted to 25 ml.

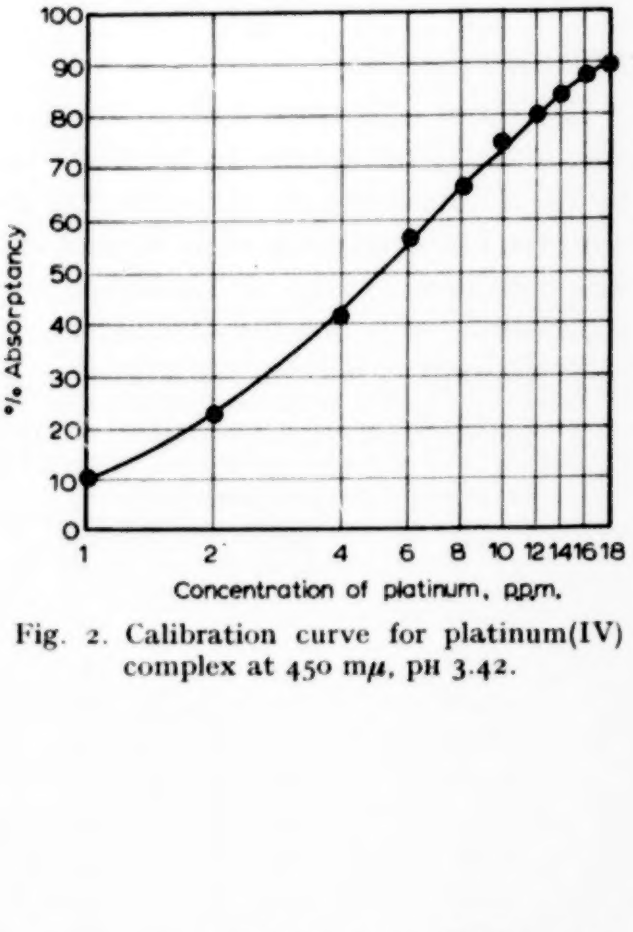

Fig. 2. Calibration curve for platinum(IV) complex at 450 mμ, pH 3.42.

Effects of pH, reagent concentration and time

In order to study the effect of pH, solutions were prepared by the addition of a fixed amount of platinum to 5 ml of the reagent and adjusting the pH's of the solutions over the range 3.42–5.90 through use of the appropriate buffers. Lower or higher pH values were obtained by adding dilute sulfuric acid or sodium hydroxide solutions. It was found that with increasing pH the absorbance of the solutions increased up to pH 3.0 and then remained constant up to pH 4.0, after which it decreased continuously. Subsequent measurements were, therefore, carried out in the pH range 3.0–4.0.

Five ml of 1% reagent solution were required for maximum development of color for 5 p.p.m. of platinum(IV). Addition of more reagent up to 7 ml did not change the absorbance of the color.

The color formed quickly on the addition of the reagent to platinum(IV) at a pH range 3–4 and maximum color developed in 25 min and remained constant up to 1 h and then decreased slightly afterwards.

Beer's law, optimum range and accuracy

The color complex obeys Beer's law for platinum(IV) concentration of 1 to 12 p.p.m. On plotting per cent absorptancy (*i.e.* 100-% transmittance) *versus* log concentration the Ringbom's[2] curve (Fig. 2) was obtained, which shows that the optimum concentration range is between 4 and 12 p.p.m. where the per cent relative error per 1% absolute photometric error, as evaluated by Ayres' equation[3], is 2.87.

Sensitivity

Sandell's[8] spectrophotometric sensitivity, as calculated from Beer's law data, is given by 0.003 μg/cm^2. This corresponds to a sensitivity of 1 part of platinum per 59,000,000 parts of the solution.

Effect of diverse ions

The effect of diverse ions on the color complex was studied by adding different amounts of ionic species to the platinum(IV) solution and then developing the color by the addition of 5 ml of the reagent solution before making up its volume to 25 ml with the buffer solution of pH 3.42. A difference of 0.005 unit in the absorbance value was considered to be an interference. It was found that tartaric acid eliminated interference of a number of ions. The tolerance limits of various ions for 8 p.p.m. of platinum(IV) with or without the presence of tartrate are given in Table I.

TABLE I

Ions	*Tartrate added p.p.m.*	*Maximum amount of ion tolerated p.p.m.*	*Ions*	*Tartrate added p.p.m.*	*Maximum amount of ion tolerated p.p.m.*
Pd^{+2}	—	16	Co^{+2}	32	16
Pd^{+2}	32	24	Ni^{+2}	32	16
Ru^{+3}	—	8	Mg^{+2}	—	16
Rh^{+3}	—	4	Mg^{+2}	32	32
Rh^{+3}	32	8	Ca^{+2}	—	16
Ir^{+4}	—	16	Ca^{+2}	32	32
Ir^{+4}	32	32	Sr^{+2}	—	16
Zn^{+2}	—	16	Sr^{+2}	32	32
Cd^{+2}	—	32	Ba^{+2}	—	16
As^{+5}	—	16	Ba^{+2}	32	32
Pb^{+2}	—	16	Th^{+4}	32	16
Mn^{+2}	—	16	Zr^{+4}	—	8
Mn^{+2}	32	32	Zr^{+4}	32	16
Cr^{+3}	—	16	UO$_2^{+2}$	32	16
Cr^{+3}	32	32	MoO$_4^{-2}$	32	16

Osmium should be separated from platinum as osmic acid by nitric acid oxidation and distillation[8] in order to avoid its interference.

Composition study of the color complex in solution

The composition of the complex in solution was studied by "continuous variation"[4] and "molar ratio"[5] methods. In both the methods, equimolecular solutions of platinum(IV) and the reagent were mixed in the proper proportions and after making up the volume to 25 ml in each case with buffer of pH 3.42, they were allowed to stand overnight for full development of color. The absorbances of the solutions were then measured at 450 mμ against water. Owing to low concentration of the reagent in dilute equimolecular solutions, overnight standing was necessary for complete color development. Results of these two methods as given in Figs. 3 and 4 show that

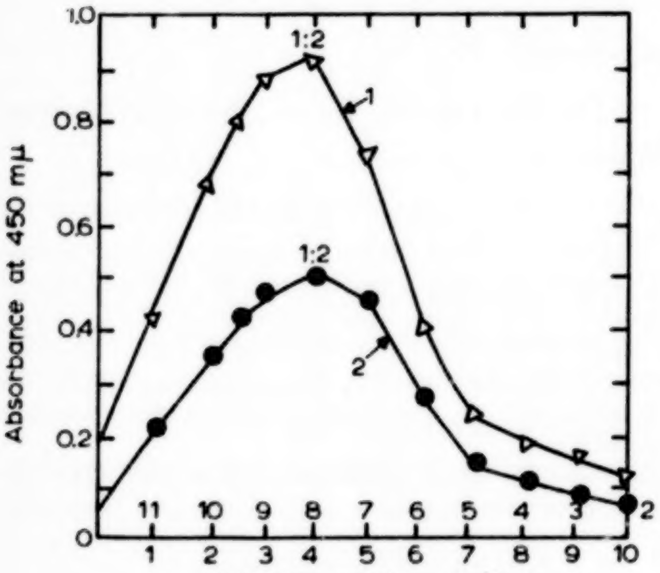

Fig. 3. Determination of the ratio of platinum(IV) to reagent by continuous variation method. Curve 1: Concn. of platinum(IV) = Concn. of reagent = $1.325 \cdot 10^{-3}$ *M*. Curve 2: Concn. of platinum(IV) = Concn. of reagent = $0.66 \cdot 10^{-3}$ *M*. Total volume in each case = 12 ml.

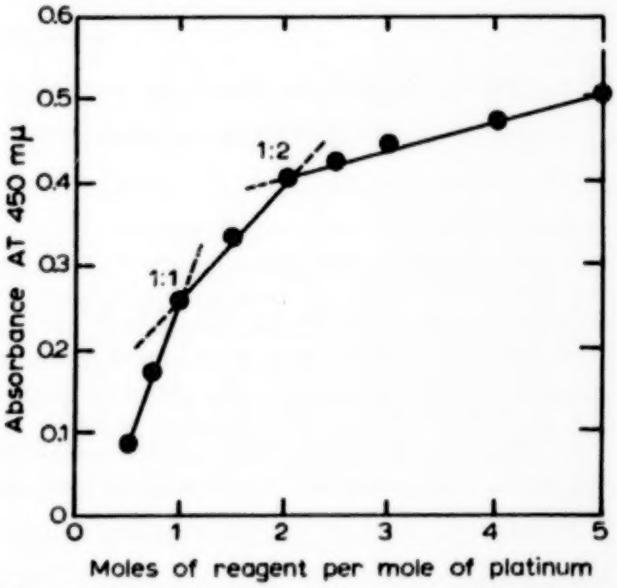

Fig. 4. Determination of the ratio of platinum (IV) to reagent by molar ratio method. Platinum(IV) concn. = $7.92 \cdot 10^{-5}$ *M* (constant) and reagent concn. varied.

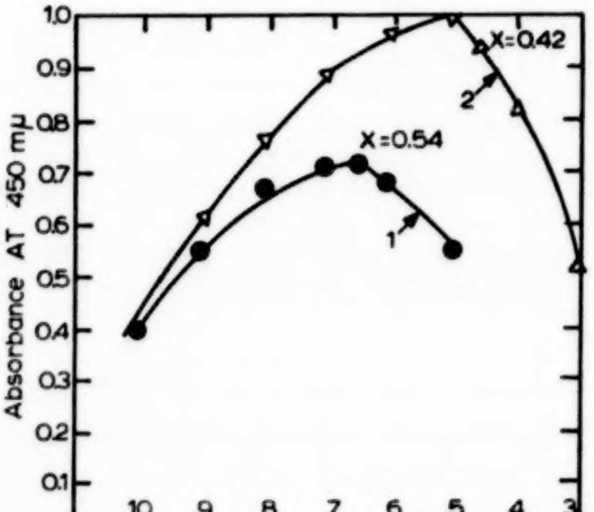

Fig. 5. Absorbance of mixtures of non-equimolecular solutions. Curve 1: $0.66 \cdot 10^{-3}$ *M* platinum(IV); $1.32 \cdot 10^{-3}$ *M* reagent solution. Curve 2: $0.66 \cdot 10^{-3}$ *M* platinum(IV); $2.64 \cdot 10^{-3}$ *M* reagent solution.

platinum(IV) forms a 1 : 2 complex with the reagent. The molar ratio method also shows (*cf.* Fig. 4) the formation of a 1 : 1 complex when the reagent is not present in excess.

Dissociation constant of the complex

The dissociation constant, K was calculated according to JOB's equation[4,7] after a study at 450 mμ of the absorption of the color complex (*cf.* Fig. 5) formed, according to procedures given under "composition study", from mixtures of non-equimolecular solutions of the reagent and platinum(IV), adjusted to pH 3.42. The average dissociation constant was thus found to be $2.3 \cdot 10^{-8}$ at room temperature.

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The author expresses his deep gratefulness to Dr. PHILIP W. WEST, Boyd Professor of Chemistry, for furnishing laboratory facilities.

SUMMARY

The orange color complex formed by platinum(IV) with *o*-phenylenediamine at the pH range 3–4 forms the basis of sensitive colorimetric method for determination of the metal. The color complex has an absorption maximum at 450 mμ and obeys Beer's law for a platinum(IV) concentration of 1 to 12 p.p.m., the optimum concentration range being 4 to 12 p.p.m. where the per cent relative error per 1% absolute photometric error is 2.87. Sensitivity of the color reaction is 1 part of platinum per 59,000,000 parts of the solution.

Continuous variation and molar ratio methods indicate that platinum(IV) forms with the reagent a 1 : 2 complex which has an average dissociation constant of $2.3 \cdot 10^{-8}$ at room temperature.

RÉSUMÉ

Le platine donne avec l'*o*-phénylènediamine un complexe coloré orange. Cette réaction peut être utilisée pour le dosage colorimétrique de cet élément.

ZUSAMMENFASSUNG

Die Reaktion von Platin mit *o*-Phenylendiamin, die unter Bildung eines orange gefärbten Komplexes verläuft, kann zur kolorimetrischen Bestimmung von Platin verwendet werden.

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VOLTAMMETRY AT INERT ELECTRODES

I. ANALYTICAL APPLICATIONS OF BORON CARBIDE ELECTRODES

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A preliminary report on the voltammetric response of B_4C ("Norbide", Norton Company, Worcester, Mass.) electrodes has been presented[1]. It has been shown that, using relatively simple analytical procedures, peak currents (i_p) for the oxidation of ferrocyanide, iron(II), and *o*-dianisidine, and for the reduction of ferricyanide and zincate at stationary B_4C electrodes were reproducible within about ± 1% mean deviation. Half-peak potentials ($E_{p/2}$) for these systems were reproducible within a few millivolts. This study presents additional data which, it is felt, places B_4C in the category of inert electrodes and leads to the conclusion that B_4C is an acceptable and versatile material for voltammetric studies.

The evaluation of a working electrode for voltammetric studies should be based on the following: (1) the availability of the proposed electrode material in suitable form and purity, (2) the response which the electrode gives in various supporting electrolytes, (3) the types of electroactive species which can be oxidized or reduced at its surface, (4) the value and constancy of half-wave or half-peak potentials, (5) the reproducibility of diffusion or peak currents, and (6) the adherence of experimental data to fundamental current–voltage relationships. The first five of these criteria are related to the potential use of the electrode in analytical applications. The sixth, while dependent upon the first five, serves as the basis for the selection of a given electrode in the study of electrode processes and mass transport phenomena.

The reasons for including the first criterion seem to be selfevident. The second establishes the "inertness" of the electrode and indicates the useful potential range over which it can be used. The third may be illustrated best by an example. Not all electrochemical species can be oxidized or reduced at any electrode. The mercury chloride film anode, introduced by KUWANA AND ADAMS[2] was suitable for the oxidation of organic species, but oxidation of certain inorganic species was not possible at its surface.

It is not necessary that half-wave potentials determined at a particular electrode agree with those determined at some other electrode. It is essential for qualitative applications however, that they remain constant, and that sufficient differentiation between the half-wave potentials of several species in solution can be achieved by judicious choice of supporting electrolyte. On the other hand, if the electrode gives values of half-wave potentials which are readily related to $E°$ values (*i.e.*, the potential of the electrode is controlled only by the ratio of oxidized to reduced species), the electrode might be considered "inert" in the classical sense. For quantitative determinations the fifth criterion must be investigated. Only those electrodes which give limiting or peak currents which are reproducible within 1 or 2% over at least a tenfold concentration range of the electroactive species will normally be acceptable as new working electrodes.

It can be seen that there is considerable interdependence between the above criteria. It is very unlikely, for example, that an electrode which gives erratic residual currents in a given supporting electrolyte will give reproducible limiting currents for an electroactive species in that solution. It is also highly unlikely that any given electrode will find universal applicability, and it is not intended that the above criteria be so interpreted. Likewise, it is not necessary that the exact manner in which an electrode functions be known. Striking examples of the latter are platinum and gold, which, while used extensively in both analytical and theoretical applications, are not understood fully in terms of the actual electron transfer process which takes place at their surfaces.

The behavior of B_4C will be considered in light of the criteria set forward. In order that a more extensive treatment of the sixth point may be undertaken, the theoretical aspects of the investigation of B_4C electrodes will be presented later.

EXPERIMENTAL

Boron carbide

Four cylindrical, hot pressed B_4C rods of 1/4", 5/16", 3/8", and 1/2" diameters were obtained from the Norton Company. According to technical data supplied by the company, the specimens were 99+% B+C and probably contained some free graphite. Spectroscopic analysis of one specimen showed the chief impurity to be calcium (present to the extent of several tenths of a percent) with traces of magnesium and silicon. Boron carbide is one of the hardest substances known and is reported to be unattacked by all common acids and bases. Concentrated nitric acid at the boiling point and moderately warm chromic acid have no apparent effect on B_4C. Although pure B_4C is a non-conductor, "Norbide" has an electrical resistivity of only 0.3–0.8 Ohm-cm at room temperature. This slight added resistance is negligible in comparison with the usual 400 to 600 Ohms associated with most polarographic circuits. Although the mode of electrical conductivity in B_4C is not known, it will be shown presently that the electroactive area of the electrode agrees quite well with the estimated geometric area; *i.e.*, the voltammetric response is a function of the B_4C matrix.

It was reasoned that the inert nature of B_4C might eliminate the problem of surface attack on an electrode during the course of an electrochemical investigation and thus lead to more reproducible analytical results and to a better understanding of electrode processes in general. Apparently because of its inert nature, few materials will bond with B_4C. Finding a suitable material for masking off unwanted portions of a rod so that a reproducible working area could be defined was one of the most difficult problems encountered in the study of B_4C electrodes. Three mounting procedures have been used successfully. The first involves placing a "Teflon" sleeve around the electrode and painting the B_4C–Teflon interface with a neoprene-base paint, "Pro-Chem" (Pro-Chem Co., New York). About ten to fifteen turns of ordinary drafting tape wound around the electrode and painted with Pro-Chem paint may be substituted for the Teflon sleeve. The end of the B_4C rod is recessed from 2 to 5 mm from the end of the tape in order to define a restricted linear diffusion path. A piece of glass tubing is sealed to the opposite end of the rod by inserting it into the Teflon sleeve or by wrapping drafting tape around the glass B_4C juncture. The glass tubing serves both as a support for the electrode and as a well for a pool of mercury. Electrical contact is established through a short length of platinum wire dipping into the mercury. It has been found that the intimate contact between B_4C and mercury provides acceptably low contact resistance. If Pro-Chem painted electrodes are allowed to age about one week before placing the mounted electrode into solution, this type of mounting can be used for several months without leakage. The disadvantage of this mounting is that, while Pro-Chem is seemingly unattacked by conc. HNO_3 and other strong acids, once used in these solutions it becomes susceptible to attack by strong bases. On the other hand, after prolonged use in basic solution, no attack is noticed when the electrode is transferred to neutral or acid solutions.

The second mounting method, not influenced by the acid–base history effect, has been used more recently. When ceresin wax is painted onto a B_4C surface a waterproof seal is obtained. After a short time, however, the wax recedes from the B_4C. If the hot wax is painted onto the end of a piece of drafting tape (adhesive side) and the tape wound around the slightly warm B_4C cylinder under hand tension, a good, lasting seal is obtained. A glass tube is mounted as described previously. Finally, all joints and exposed tape are painted with ceresin wax. Photographs of two of these mountings are reproduced in Fig. 1.

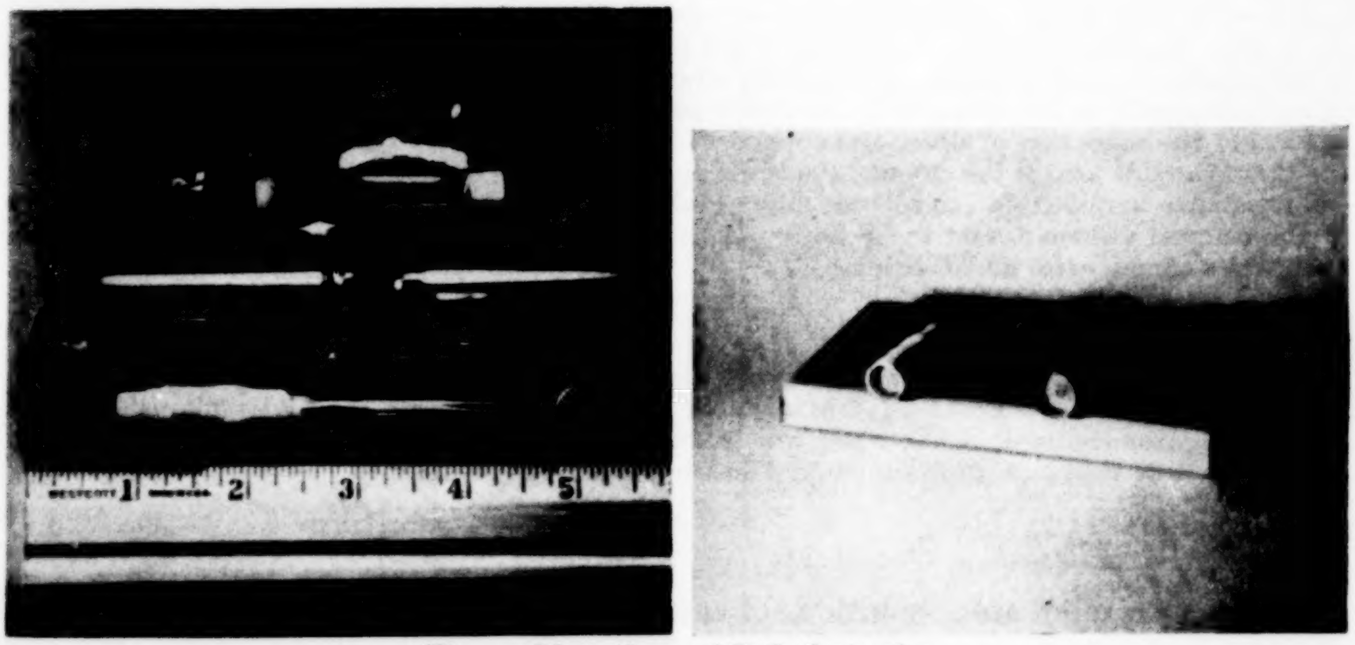

Fig. 1. Mountings of B_4C electrodes.

A third mounting, limited somewhat in application, is the most easily used. Drafting tape is wound around the electrode and is allowed to project about 2 to 5 mm beyond the working face of the electrode. Only the end of the coil of tape and the outside of the tape are painted with hot ceresin wax. No wax is actually in contact with the B_4C. The adhesive on the tape forms a waterproof seal with the B_4C. Apparently no contaminants are extracted from the tape in aqueous solution. Since the tape is wound around the cylinder, and no soft wax comes in contact with the working surface of the electrode, very reproducible areas can be obtained for successive mountings. If materials are electrolyzed which require conc. HNO_3 or chromic acid treatment to remove their oxidation or reduction products, the tape can be removed, the electrode cleaned and remounted easily. The cleaned B_4C electrode has the advantage over platinum or gold in that its electroactive area is not changed by such treatment, and no waiting period for the stripping of oxides is necessary.

Before mounting a new B_4C specimen, the rod is rinsed with CCl_4 to remove a thin film of oil presumably left from the manufacturing process. The film is not removed by hot, conc. HNO_3, but evidences itself by an increase of several hundred Ohms in the cell circuit. The CCl_4 rinsing is followed by cleaning for one or more hours in hot, conc. HNO_3. The electrode is then rinsed with distilled water, dried, and mounted.

One of the four specimens showed initially high residual currents in all supporting electrolytes. On the assumption that surface impurities might be present, the electrode was first polished (by lapping with 8 μ diamond compound) followed by anodic stripping in *M* HNO_3 at 1.00 V applied for 36 h. After stripping, the electrode gave very low background polarograms which were essentially flat in the usable potential range. The three other specimens were used in the "as received" condition following the initial cleaning procedure described previously. Background currents were only slightly higher with the latter electrodes.

Apparatus

With the exception of a few scans made with an external scanner all current-voltage curves were recorded with the Leeds and Northrup Electrochemograph at a scan rate of 200 mV/min. The polarographic cell consisted of a 50-ml beaker cut off just below the lip. A piece of 3/8" thick Lucite with holes of the appropriate sizes served to support the electrodes, a gas dispersing tube, and a glass electrode. The rim of the beaker was brought into contact with the Lucite to isolate the polarographic solution from the atmosphere when cathodic reductions were studied. A saturated calomel electrode of the side-arm type with a saturated KCl salt bridge was used in most of the work. For the reduction of silver and copper a 1 *M* KNO_3 bridge was used. A filter paper plug in the tip of the side arm of the calomel electrode prevented rapid drainage of electrolyte. The overall cell resistance varied from 450 to 1000 Ohms and was found to depend chiefly upon the condition of the calomel electrode and the porosity of the plug. The cell resistance was measured before each series of runs with an AC bridge.

Chemicals

All inorganic chemicals were reagent grade and were used without further purification. The organic chemicals were Eastman White Label grade with the exception of *o*-dianisidine and 1-nitro-3-benzene sulfonic acids, which were kindly supplied through the courtesy of John Tinker, E.I. DuPont de Nemours and Company. The 1-naphthol was resublimed.

Operating procedure

500 to 1000 ml of stock solutions of each electroactive species were prepared with deaerated, distilled water. The ferrocyanide solutions were further deaerated and stored under nitrogen in black bottles. Supporting electrolytes of 1 or 2 *M* concentration were prepared and deaerated with nitrogen. For all anodic work, appropriate aliquots of each solution were pipetted into a volumetric flask and brought to the mark with deaerated, distilled water. These solutions were used without further deaeration. For cathodic reductions the solutions were prepared in the same manner and again deaerated after placing them into the polarographic cell.

The B_4C electrode was rinsed with distilled water, excess water blown off and the electrode placed into the polarographic cell. No further pretreatment was normally employed. In the event that a film formed during the course of electrolysis, the film was removed with an appropriate solvent or oxidized with HNO_3 or chromic acid followed by a rinse with distilled water. After the electrodes were in place and any necessary deaeration terminated, the starting voltage was applied. A period of one minute was allowed for the system to come to equilibrium. Current–voltage curves were then recorded starting about 200 mV from the foot of the wave. By using such starting voltages it has been found that, in most cases, linear extrapolation of the residual current line to the peak potential gives a value of i_{res} which agrees within ± 0.02 μA of that obtained on a background scan. All current–voltage curves were determined at stationary electrodes with upward diffusion of the electroactive species.

No attempt was made to control the temperature of the electrolytic solution in early stages of the work. Rather, the temperature of each solution was measured and the polarograms were corrected on the basis of independently determined temperature coefficients when the temperature was not 25°. More recently, the experiments have been carried out in a thermostated water bath at 25.00° ± 0.05°.

Electrode areas were determined from the rearranged linear diffusion equation

$$A = \frac{(it^{1/2})\ \pi^{1/2}}{nF\ D^{1/2} C^{b}_{ox}} \tag{1}$$

where A is the area in cm², i is the current in amperes, t is the time in sec after initiation of the electrolysis, n is the number of electrons involved in the reaction,

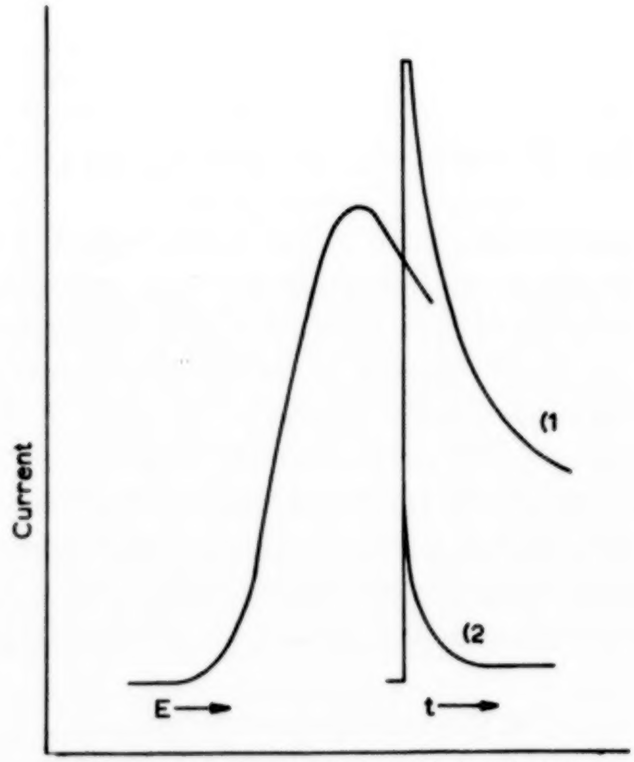

Fig. 2. Method of determining $(it^{1/2})$.

F is the Faraday and C^{b}_{ox} is the concentration of the electroactive species in moles-cm^{-3} in the bulk of the solution. The product $(it^{1/2})$ was obtained by recording the current decay with time at an applied voltage about 50 mV beyond the peak potential of a normal polarogram (curve I, Fig. 2). Correction for background current was made by recording the current–time curve at the same applied voltage for the supporting electrolyte (curve 2, Fig. 2) and subtracting curve 2 from curve 1 point by point.

The oxidation of 10^{-3} M $K_4Fe(CN)_6$ in 0.5 M KCl was used to determine all electrode areas using the D value of $6.39 \cdot 10^{-6}$ cm²/sec given by VON STACKELBERG[3]. Typical constancy of $(it^{1/2})$ with time for the oxidation of ferrocyanide in 0.5 M KCl is shown in Table I. In order to read the recorded i–t curve with the greatest accuracy, a high recorder sensitivity is employed. Thus, when the voltage is applied to the electrode, the initial surge of current overdrives the recorder amplifier. Recovery of the amplifier and recorder pen requires about 10 sec. Also, in the initial stages of electrolysis, the electrode potential has not yet attained the value of the applied potential.

TABLE I

CONSTANCY OF $(it^{1/2})$ WITH TIME FOR $K_4Fe(CN)_6$ IN 0.5 M KCl

Rough	*B_4C-A*	*Polished*	*B_4C*
t, sec	*$it^{1/2}$*	*t, sec*	*$it^{1/2}$*
12	23.8	12	50.7
15	23.8	15	50.3
18	23.9	18	50.2
21	24.0	21	50.1
24	24.0	24	49.9
27	23.9_5	27	50.0
30	24.0	30	50.2
45	24.0	33	50.2
60	23.9_5	36	50.2
120	23.9	39	50.3
		42	50.4
		45	50.5
		60	51.1

Therefore, currents during the first 15 to 20 sec do not reflect behavior in accord with equation (1). At long periods of electrolysis convection undoubtedly becomes important and stirring in the vicinity of the electrode causes an increase in $(it^{1/2})$.

It is recognized that i–t curves should be recorded at constant electrode *potential* rather than at a fixed *applied voltage*. However, in view of the reasonable results obtained, changes in electrode potential after the first 20 sec of electrolysis appear to introduce no serious error at this level of accuracy. The fact that $(it^{1/2})$ values are constant for a short period of time seems to indicate that linear diffusion conditions are attained in this interval with this electrode configuration. A more detailed treatment of linear diffusion processes at B_4C electrodes will be presented in Part II.

RESULTS AND DISCUSSION

Some of the systems studied at B_4C electrodes are listed in Table II. Half-peak potentials are compared with literature values of half-wave or half-peak potentials where these values are available. The systems studied were chosen to represent ion–ion or molecule–ion oxidations and reductions of organic and inorganic species over most of the useful potential range of the electrode. In addition, several metal ion reductions were carried out to demonstrate the utility of the electrode for depositions.

Peak-type current–voltage curves were obtained for all systems listed. These showed the expected dependency upon concentration of electroactive species, n values, reversibility of the electrode reaction, pH, variation of temperature, and scan rate. Tracings of some original current–voltage curves are reproduced in Fig. 3.

Half-wave potentials in Table II are followed by the range of potentials where more than 8 determinations were made. The other values indicate the mean of no less than four determinations. All values are *versus* SCE at 25°.

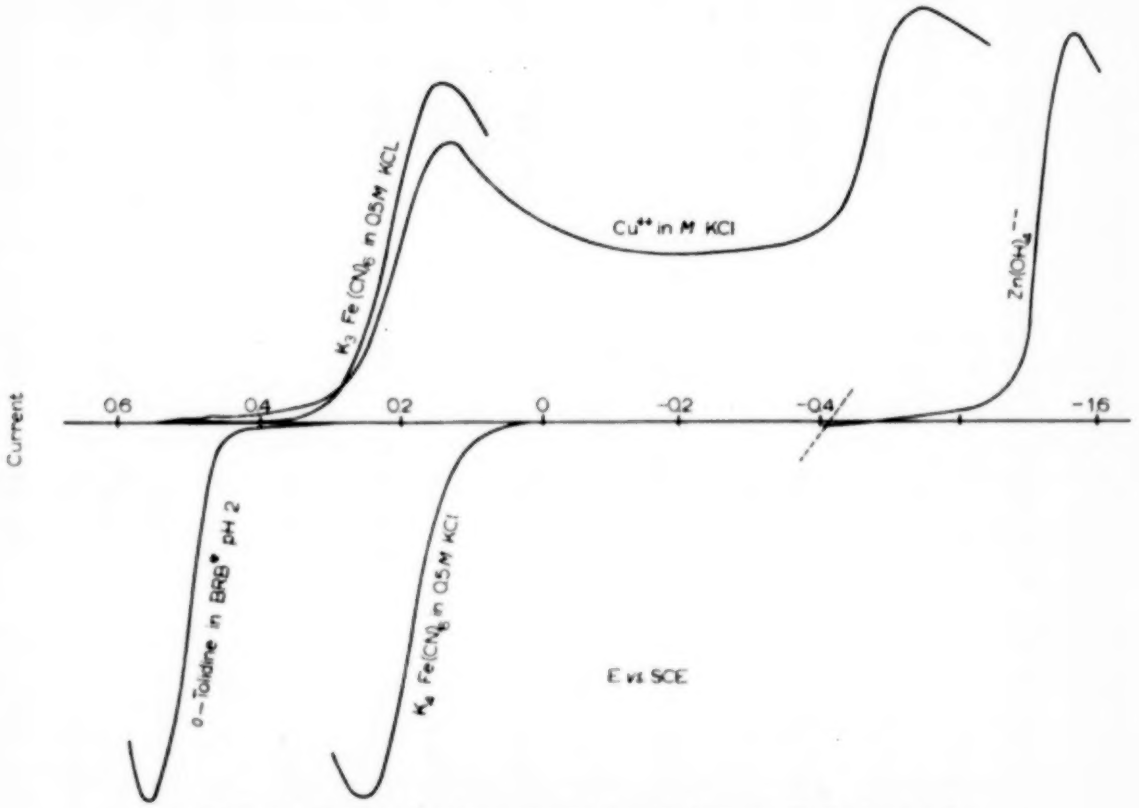

Fig. 3. Typical polarograms at stationary B_4C electrodes.
* Britton-Robinson buffer.

In addition to the systems listed in Table II, the oxidation of N,N-dimethyl-*p*-phenylenediamine (DPP) was studied as a function of pH. A plot of $E_{p/2}$ *vs.* pH was linear from pH = 0 to 5.77. A least squares treatment of the data for DPP gave the following empirical equation for $E_{p/2}$ over this pH range.

$$E_{p/2} = +0.530 - 0.059_6 \text{ pH} \pm 0.002_5 \text{ V } vs. \text{ SCE}$$

Extrapolation of the data of MICHAELIS AND HILL[4] to pH = 0 gives $E° = 0.524$ V. A manual current–voltage curve for the oxidation of $2 \cdot 10^{-4}$ *M* ferrocyanide in 0.5 *M* KCl at an "as received" electrode gave an $E_{p/2}$ of + 0.210 V *vs.* SCE. KOLTHOFF AND TOMSICEK[5] obtained a formal potential of + 0.4581 V *vs.* normal hydrogen electrode for an equimolar mixture of $4 \cdot 10^{-4}$ *M* ferro- and ferricyanide in 0.5 *M* KCl by potentiometric methods. Their value corresponds to + 0.212 V *vs.* SCE. In general, agreement between half-peak potentials at B_4C electrodes and those obtained at other solid electrodes is quite good.

The oxidation of potassium ferrocyanide in 0.5 *M* KCl was chosen as a calibration and comparison system for B_4C electrodes. The ferro-ferricyanide system is reversible, $n = 1$, and diffusion coefficients[3] are known in KCl. Since the temperature of the electrolytic solutions was not controlled, temperature coefficients of $E_{p/2}$ and i_p were required. These were obtained by thermostating the cell at a number of temperatures

TABLE II

OXIDATIONS AND REDUCTIONS AT B_4C ELECTRODES

Electroactive species	*Supporting electrolyte*	*Wave form*	$E_{p/2}$ *vs. SCE*	*Literature values*	*Ref.*
A. Inorganic					
$K_4Fe(CN)_6$ (ox)	0.5 *M* KCl	w.d.[a]	+0.198 ± 0.005	+0.203	8
$K_3Fe(CN)_6$ (red)	0.5 *M* KCl	w.d.	+0.226 ± 0.002	+0.222	8
I^- (ox)	*M* H_2SO_4	w.d.	+0.500 ± 0.003	+0.502,0.50	9,10
IO_3^- (red)	*M* H_2SO_4	f.w.d.[b]	+0.05	—0.05	11
Ag^+ (red)	0.1 *M* KNO_3	w.d.	+0.19	+0.10(1·10⁻⁵ *M*)	12
			(2·10⁻⁴ *M*)	+0.21(1·10⁻⁴ *M*)	13
Sn^{+2} (red)	4 *M* NH_4Cl–*M* HCl	w.d.	—0.73		
	M KCl	w.d.	—0.595 ± 0.005		
	M HCl	w.d.	—0.619 ± 0.003		
Pb^{+2} (red)	0.1 *M* KNO_3	w.d.	—0.58	—0.451	12
Cu^{+2} (red)	*M* KCl	w.d.	+0.218 ± 0.001	+0.220	8
	pH = 3 to 4	(first wave)			
	0.5 *M* KCl	w.d.	+0.16 (first wave)	+0.185	8
	pH = 4.4 to 5.4		—0.48(second wave)		
	0.5 *M* Na_3Cit	no peak	—0.28		
	pH = 4.6				
	M H_2SO_4	w.d.	—0.09		
	0.1 *M* $Na_4P_2O_7$	w.d.	—0.208 ± 0.002		
	pH = 4.7				
Fe^{+2} (ox)	*M* HCl	w.d.	+0.456 ± 0.005	+0.463, 0.453	14, 19
$Zn(OH)_4^{-2}$ (red)	0.1 *M* NaOH	w.d.	—1.522 ± 0.005		

TABLE II (continued)

Electroactive species	*Supporting electrolyte*	*Wave form*	*$E_{p/2}$ vs. SCE*	*Literature values*	*Ref.*
Tl^+ (red)	0.1 *M* KCl	w.d.	—0.87		
	1 *M* NaOH	w.d.	—0.97		
(ox)	1 *M* NaOH	f.w.d.	+0.22		
Tl_2O_3 (red)	1 *M* NaOH	w.d.	—0.26	—0.23 ± 0.02	15
Mn^{+2}(2e, MnO_2) (ox)	0.1 *M* HAc	f.w.d.	0.97		
B. Organic					
N-dimethylaniline (ox)	BRB-"A" pH = 2.4	w.d.	+0.73	+0.68	18
	0.2 *M* in Na_2SO_4	film			
o-dianisidine (ox)	*M* H_2SO_4	w.d.	+0.587 ± 0.002	+0.59	16
p-aminodiphenylamine	BRB"A" pH = 2.4		+0.361 ± 0.001		
(ox)	0.2 *M* in Na_2SO_4				
1-nitro-3-benzene	0.2 *M* KCl–HCl Buff.	w.d.	—0.485 ± 0.005		
sulfonic acid (red)	pH = 1.7				
8-hydroxyquinoline	BRB"A" + 0.2 *M* KCl		—1.16	—1.03	17(DME)
	+ trace ethanol				
thioglycerol	BRB 0.2 *M* Na_2SO_4	w.d.	+0.160 ± 0.003		
	pH = 2.6	film			
α-napthol	BRB"A" +0.2 *M* Na_2SO_4	film	+0.54	+0.63	18
	pH = 2.4				
o-tolidine	1 *M* HCl	f.w.d.	+0.657 ± 0.001		

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* $E_{p/2}$, $E_{1/2}$, $E_{1/4}$ values
[a] well defined
[b] fairly well defined

between 22 and 32 degrees and plotting the values of $E_{p/2}$ and i_p obtained from current–voltage curves against temperature. From these plots a temperature coefficient of -1.6 mV/deg was deduced for $E_{p/2}$ and $+0.497$ µA-l/mole/cm²/deg for i_p. Applying the temperature correction to 207 experimental $E_{p/2}$ values at four different electrodes, a value of $E_{p/2} = +0.198 \pm 1$ mV at the 95% confidence level was obtained. No $E_{p/2}$ deviated by more than 5 mV from this mean. The temperatures at which the original data were obtained varied from 22.7° to 32.2°. The ferrocyanide concentration ranged from 0.5 to $20 \cdot 10^{-4}$ M. Later work (about 100 determinations) carried out in a constant temperature bath at 25.0° confirmed the value of 0.198. Half-peak potentials were independent of the B_4C specimen used. The temperature coefficient of i_p agrees quite well with the 6% increase in i_p between 25° and 30° noted by NICHOLSON[6].

The area of each electrode was determined as described in the experimental section of this paper. The reproducibility of the product ($it^{1/2}$) at any given electrode from day to day was about 0.5%. For different electrodes, or for successive mountings of the same electrode, an estimate of the various additive errors involved leads to the conclusion that the overall accuracy of the method is about ± 5%. To test the applicability of the method the area of a B_4C electrode was determined from the oxidation of ferrocyanide in 0.5 M KCl. It was found to be 0.373 cm². The reduction of ferricyanide in 0.5 M KCl at the same electrode provided an ($it^{1/2}$) product from which an area of 0.367 cm² was calculated. The difference between these two values is less than 2%.

TABLE III

COMPARISON OF GEOMETRIC AND ELECTROCHEMICAL AREAS

Electrode	*Geometric area*	*Electrochemical area*
Polished	0.36	0.36$_3$
Rough-A	0.18	0.19$_3$
Rough-B	0.44	0.53$_1$
Rough-C	0.7	0.94$_2$

Four electrodes were mounted and their areas determined from i–t curves. Table III shows the agreement between estimated geometric areas and the corresponding areas determined from i–t curves. All of these electrodes were mounted with Pro-Chem. Consequently, the defined working area was irregular. Geometric areas were calculated as if the working areas were circles using the mean of about ten diameters on each electrode. No "roughness factor" was introduced although three of the electrode surfaces were quite grainy in appearance. The largest electrode had a slightly raised "O" on its surface.

During a period of six months over 400 current–voltage curves for the oxidation of $K_4Fe(CN)_6$ in 0.5 M KCl were recorded at the four B_4C electrodes. The polished electrode was twice remounted. The rough specimens were used in their original mountings for about three months (Pro-Chem sealant). The first two mountings of the polished electrode gave identical areas of 0.363 cm². The third mounting (of the second kind discussed in the experimental section) had an area of 0.464 cm². Concentrations of 2, 4, 6, and $10 \cdot 10^{-4}$ M ferrocyanide were used. Peak currents were corrected to 25.0°. Peak currents were also corrected according to DELAHAY'S equation[7] for the decrease in peak current associated with change in scan rate from IR drop in the cell circuit.

Values of i_p/CA for all determinations were within the estimated accuracy of the area determination. It should be borne in mind that, for analytical applications (where one electrode area is used for long periods of time), the precision is considerably better than might be deduced from the reproducibility of i_p/CA for several electrodes. Peak currents for the oxidation of ferrocyanide have a short-term reproducibility of 0.5 to 0.7% and a long-term reproducibility of about 1 to 1.5%. The day-to-day reproducibility of two electrodes is shown in Table IV.

TABLE IV

DAY-TO-DAY REPRODUCIBILITY OF B_4C ELECTRODES
OXIDATION OF 10^{-3} M $K_4Fe(CN)_6$ IN 0.5 M KCl
(i_p corrected to 25°)

Date	*Polished electrode* i_p/CA	*Rough electrode-A* i_p/CA
5-16-59	37.0	—
6-20-59	37.7	37.4
6-22-59	—	38.2
6-23-59	37.45	38.1
6-24-59	—	38.2
7-14-59	37.4	—
Mean	37.4	38.0
Mean deviation	1.02%	1.6%

Copper

The reduction of cupric ion was carried out in a number of supporting electrolytes. Very good waves were obtained in M KCl, 0.5 N KCl, and M NH_3–M NH_4Cl, for the reduction to the cuprous state. The second wave in these media was well defined, but i_p reproducibility was no better than 3% (variations in 0.5 M KCl were as much as 30% for $2 \cdot 10^{-5}$ M cupric) and the half-peak potentials were reproducible to only 10 to 15 mV. The first wave in 1 M KCl was reproducible to $\pm 0.8\%$ for concentrations of $2 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ M cupric ion. Thorough deaeration of the solutions was necessary in order to obtain this level of reproducibility.

Two reduction waves were also obtained in N HCl, but the first is very drawn out with an apparent $E_{p/2}$ at about 0.0 V. The second wave is well defined, but i_p is not reproducible to better than 10%. Two-electron reductions occur in M H_2SO_4 and 0.1 M $Na_4P_2O_7$ at pH = 4.7. Waves in both of these supporting electrolytes are well defined, half-peak potentials are reproducible to ± 2 mV, and i_p is reproducible within ± 3%. Tartrate and citrate media gave very poorly-defined waves not suitable for analytical applications.

Thallium

Thallous was reduced at B_4C in 0.1 N HAc, 0.1 and 1.0 M KCl, and 1 M NaOH solutions. Thallous oxidized in 1 N NaOH at $E_{p/2} = +0.22$ V and Tl_2O_3 reduces in this medium at $E_{p/2} = -0.26$ V *vs.* SCE. Thallous ion does not oxidize in 0.1 *N* acetic acid at B_4C before background. Even if the potential is set several hundred millivolts beyond the onset of the anodic background process, no thallic formation is observed. If, however, a known amount of manganous ion is introduced into the solution, a peak-type current–voltage curve is obtained which is of considerably greater height than that obtained for the oxidation of the same concentration of manganous ion alone. The nature of this process is being investigated currently.

Background currents

To date there is no reason to believe that limiting background processes at B_4C electrodes differ from those observed at conventional electrodes. No stripping currents have been noted when the electrode potential has been set at high anodic values for prolonged periods of time and then scanned cathodically. Pretreating the electrode at high positive or high negative potentials has no effect on the half-peak potentials or peak currents. This is not, in itself, conclusive evidence that no oxides (or other oxidation products of B_4C or trace impurities) are formed on the surface of the electrode during the course of electrolysis. The reproducibility obtained with B_4C electrodes, though, leads to the conclusion that if such "oxide films" are formed, their formation takes place much more reproducibly than at platinum or gold. Background currents at B_4C electrodes are reproducible within ±0.01 μA.

Conclusions: The voltammetric response of B_4C electrodes appears to be excellent for a wide variety of electroactive materials. Present mounting procedures leave something to be desired, particularly for applications in non-aqueous solvents. An all-glass mounting would be ideal, but no suitable bond has yet been achieved between B_4C and glass. Likewise, mounting methods have limited the use of the electrode to stationary configurations. The low and reproducible background currents experienced at B_4C electrodes should make this electrode useful in amperometry, coulometry, potentiometry, and, in short, for any electrochemical investigation where the combination of low residual currents and good reproducibility are important.

ACKNOWLEDGEMENTS

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SUMMARY

Certain criteria for the evaluation of a working electrode for voltammetry have been set forth and the B_4C electrode evaluated accordingly. Inorganic and organic ion–ion and molecule–ion oxidations and reductions as well as metal depositions have been investigated using the B_4C electrode. In general, residual currents are small, half-peak potentials are reproducible and agree with literature data within a few millivolts. Peak currents can be measured with a precision of about 1%. The B_4C electrode appears to function as an "inert" electrode. The only system which failed to respond at B_4C was the oxidation of thallous in 0.1 *N* acetic acid. Present mounting methods seem to impose the most serious limitation on the applicability of B_4C electrodes.

RÉSUMÉ

Une étude a été effectuée sur les applications analytiques d'électrodes au carbure de bore, en particulier pour des dosages voltammétriques d'oxydo-réduction. Une telle électrode peut être considérée comme une électrode inerte.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Anwendbarkeit der B_4C Elektrode für voltammetrische Bestimmungen von Oxydations-und Reduktionsreaktionen. Es werden Angaben gemacht über die Reproduzierbarkeit der Elektrodencharakteristik. Die B_4C Elektrode kann als ,,inerte'' Elektrode angesehen werden.

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EFFECT OF ORGANIC AND AQUEOUS SOLVENTS ON FLAME PHOTOMETRIC EMISSION AND ATOMIC ABSORPTION SPECTROSCOPY

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It has been observed that the use of an organic solvent instead of an aqueous solvent in flame photometry considerably enhances the emission signal from a dissolved metal[1–4]. Twenty-fold increases in intensity are common, but claims up to a thousand-fold have been made[5].

The mechanism of this enhancement is not yet clearly understood. It is generally believed that it is a temperature effect. The basis for this belief is that aqueous solutions cool the flame, but organic solutions would increase flame temperature. Directionally, these effects would produce the results observed; *i.e.*, a cooler flame emits a less intense signal. However, the extent of enhancement by organic solvents cannot be explained by this hypothesis.

WAVE MECHANICS

Flame photometry

The intensity of an emitted spectral line is described by the equation:

$$S = \frac{N_2E}{\tau} = \frac{N_1E}{\tau}\,\frac{g_1e^{-E/kT}}{g_2} \qquad (1)$$

where: S = Strength of spectral line
N_2 = No. of atoms in excited state N_2 (*i.e.*, atoms which emit)
N_1 = No. in lower energy state, *i.e.*, ground state for most strong lines (these atoms cannot emit)
E = Energy differences between N_2 and N_1
also: E = $h\nu$, h being Plank's constant, ν the wave number of the line.
g_1/g_2 = Statistical weights or *a priori* probabilities
k = Boltzman's constant
T = Temperature
τ = Life time of the excited atoms

The number of excited atoms N_2 is described by the Einstein–Boltzman relation:

$$\frac{N_2}{N_1} = \frac{g_1e^{-E/kT}}{g_2} \qquad (2)$$

These equations can be interpreted as meaning that the strength of the spectral line is proportional to the number of excited atoms, and this in turn is related to the temperature of the system. It is known that using an organic solvent will give a flame approximately 500° hotter than when an aqueous solution is used (*i.e.*, 3500°K compared to 3000°K). In order to get an idea of the magnitude of intensity increase on raising the temperature from 3000°K to 3500°K we can simplify equation (1) to

$$S = \frac{N_2E}{\tau} = Be^{-E/kT} \qquad (3)$$

where B is a constant for a given spectral line. From this, at temperature T_1 and T_2:

$$\frac{S_{T_1}}{S_{T_2}} = \left(\frac{N_2E}{\tau}\right)_{T_1} \div \left(\frac{N_2E}{\tau}\right)_{T_2} = \frac{(N_2)_{T_1}}{(N_2)_{T_2}} \qquad (4)$$

i.e., the ratio of the intensity of the spectral lines at T_1 and T_2 is the same as the ratio of excited atoms at these same temperatures. It can also be derived from equation (2) that

$$\log Q = \frac{-5040\ V}{T} \qquad (5)$$

where V = E expressed in electron volts

$$Q = \frac{N_2g_2}{N_1g_1} = \frac{\text{excited atoms}}{\text{ground state atoms}} \times \frac{g_2}{g_1}$$

Let us now examine the effect on a given spectral line of varying the temperature from 3000°K to 3500°K, assuming $g_2/g_1 = 1$. When $g_2/g_1 \neq 1$ a small correction is necessary in the determination of the actual number of excited atoms at a given temperature, but not in the ratio at two different temperatures.

Case I: Temp. = 3000°K, spectral line λ = about 2000 Å
$\bumpeq$ 6 electron volts

$$\therefore \quad \log Q \bumpeq \frac{-5040 \times 6}{3000}$$

$$\bumpeq -10$$

i.e., N_2 (excited atoms) $= 10^{-10} \cdot N_1$ at 2000 Å and 3000°K
Temp. 3500°K (same spectral line)

$$\log Q = \frac{-5040 \times 6}{3500}$$

Case II: for $\lambda = 3000$ Å $\quad V = 4$ electron volts
when $T = 3000$°K $\quad N_2 = 10^{-6.7} \cdot N_1$
$T = 3500$°K $\quad N_2 = 10^{-5.9} \cdot N_1$

Case III: for $\lambda = 6000$ Å $\quad V = 2$ electron volts
when $T = 3000$°K $\quad N_2 = 10^{-3.3} \cdot N_1$
$T = 3500$°K $\quad N_2 = 10^{2.93} \cdot N_1$

These results are summarized as follows (Assuming $N_1 \rightarrow \Sigma(N_1 + N_2 + N_3 \text{---})$ where N_2, N_3, etc., are excited states.):

λ A	N_2		Ratio	
	$T_{3000°K}$	$T_{3500°K}$		Enhancement
2000	10^{-10}	$10^{-8.57}$	$\frac{1}{3.7 \cdot 10^8} \div \frac{1}{10^{10}}$	$\bumpeq$ 30-fold
3000	$10^{-6.67}$	$10^{-5.71}$	$\frac{1}{5.1 \cdot 10^5} \div \frac{1}{4.6 \cdot 10^6}$	$\bumpeq$ 9-fold
6000	$10^{-3.33}$	$10^{-2.95}$	$\frac{1}{9 \cdot 10^2} \bumpeq \frac{1}{2.1 \cdot 10^3}$	$\bumpeq$ 2.3-fold

These show clearly that a 30-fold enhancement would only be encountered with lines of about 2000 Å, but at wavelengths > 3000 Å, the enhancement would be considerably less.

Further, the calculations indicate that at short wavelengths the degree of thermal excitation would be very low and that it would probably be difficult to detect these lines. This raises the question of what excites the strong spectral lines observed in emission spectrography at these short wavelengths.

Atomic absorption

With atomic absorption we have a different system. In principle, we pass a steady beam of light through a flame in which the sample is burning. Metal atoms absorb at characteristic wavelengths. The degree of absorption is a measure of the amount of metal present. This can be used as the basis of analysis of the metal. Under ideal conditions the absorption laws hold and

$$I_\nu = I_0 e^{-K\nu l} \tag{6}$$

I_0 = Initial intensity of light
I_ν = Intensity after absorption (at wave number ν)
K_ν = Absorption coefficient
l = 'Cell' length (in this case a flame)

For a given system, K_ν determines the amount of light absorbed. It is described as follows:

$$K_\nu d\nu = \frac{\pi e^2}{mc} N_\nu f \tag{7}$$

m = Mass of the electron
e = Charge of the electron
c = Speed of light
f = Oscillator strength
N_ν = Number of atoms which can absorb a wave band between and $\nu + d\nu$

For a given spectral line, the only controllable variable in this equation is N_ν. The most useful wavelengths for atomic absorption are those associated with the atom in the ground state; hence, we can confine our arguments to unexcited atoms. It will also be noted from (6) and (7) that the degree of absorption shows no direct dependence on temperature.

Comparison between absorption and emission

It can be seen that the two systems, emission and absorption, are complementary. In emission we measure the excited atoms (in a flame $< 1\%$ of the total usually) but in absorption we measure the unexcited atoms, *i.e.*, 99% of the atoms.

This would lead us to believe that any variable, such as temperature, which enhances one phenomenum (emission) would decrease the extent of the complementary phenomenum (absorption). As the number of excited atoms increase (emission) the number of unexcited atoms (absorption) should decrease in a given population. However, this was observed not to be the case when organic solvents were used, *i.e.*, both signals increased. This indicated that the effect of the solvent was not simply to change the temperature of the flame.

EXPERIMENTAL OBSERVATIONS

The effect of various solvents on the intensity of the nickel 3414 Å emission line was examined.

Preparation of solution

Nickel solutions were made up by dissolving nickel naphthenate ("Nuodex" spectrographic standard) in benzene, such that 1 ml of benzene solution contained 500 μg of Ni. The solvent solution of nickel was then prepared by adding 5 ml of benzene solution to 45 ml of the solvent, resulting in a 50 p.p.m. solution of nickel. Solution of the nickel in benzene was necessary in order to keep it in solution in the various organic compounds. Similar blank solutions were made up which contained no nickel.

Experimental

Using an oxy-cyanogen flame to atomize and excite the solution, the emission intensity at 3414 Å was measured. After correcting for the blank, and the difference in aspiration rates, the following values were obtained.

TABLE I

EFFECT OF SOLVENT ON INTENSITY OF NICKEL EMISSION

Solution contained 50 p.p.m. Ni; intensities are corrected for feed rate.

Solvent	*Relative intensity of Ni 3414 Å line*
acetone	18
n-pentane	19
methanol	19
n-octanol	33
methyl cyclopentane	14
n-hexyl ether	20
nitrobenzene	30
toluene	16
ethyl acetate	19
cyclohexane	25
acetylacetone	20
ethylene chloride	17
monochlorobenzene	14
xylene	17
monochlorobenzene	27
methyl ethyl ketone	16
benzene	19
carbon tetrachloride	14
ethanol	19
varsol (Petroleum Solvent)	37
water	4

These intensities are relative and dependent on the part of the flame examined.

Effect of solvent on atomic absorption measurements

Using similar solutions to those described above, the degree of absorption by the nickel 3414 Å line was measured. The results are listed in Table II.

TABLE II

Solvent	*Absorption signal*
acetone	144
n-pentane	66
methanol	49
methyl cyclopentane	34
n-hexyl ether	54
nitrobenzene	72
toluene	61
ethyl acetate	31
cyclohexane	36
acetylacetone	48
ethylene chloride	30
monochlorobenzene	36
xylene	30
methyl ethyl ketone	48
benzene	42
carbon tetrachloride	65
ethanol	34
water	4

These figures give the relative strength of the absorption. They are susceptible to change with flame position since the combustion pattern varies, *i.e.*, different solvents liberate metal atoms at different speeds at different parts of the flame. If the solvent is incompletely burned, it interferes seriously with the absorption by the metal. This could be a serious source of error, and care must be taken to take measures to eliminate it. Under optimum conditions the solvent should be burned completely, leaving only the metal atoms and the products of combustion.

CONCLUSIONS

It can be seen that the use of organic solvents enhances both emission and absorption intensity of the nickel 3414 line. If the effect of the solvent is merely to increase the flame temperature, the enhanced absorption cannot be explained because the number of atoms in the ground state has decreased at the elevated temperature. This should result in a slight loss in sensitivity.

In view ot the experimental observations, an alternate mechanism for this process is proposed. This is outlined below.

SUGGESTED MECHANISM OF SIGNAL ENHANCEMENT BY ORGANIC SOLVENTS

Part of the definition of atomic spectra is that the energy is emitted by atoms. But the formation of these atoms is an important rate controlling step in the process. Let us consider a metal dissolved in *aqueous solution*. First it is ionic, and second, it is almost certainly hydrated. When it is introduced into the flame, it exists for a short period at least in a water droplet and, unlike the water, it is not very volatile. This means that after the water in the droplet has all been evaporated, the hydrated metal ion remains. This ion must be dehydrated before the atomic state is regained. Even when it is reduced to the solid state it will be appreciated that any other metal present in the origin solution will be present in the residue, and could conceivably "lock in" the atoms in the very small semi-crystalline residue. This residue must be broken up and atoms released. After the metal becomes atomic, it must be excited before it emits a spectrum.

The entire process of forming free metal atoms from aqueous solution is endothermic and requires a finite time and considerable energy. It is likely that much of the metal in solution will pass through the flame and never get to the excited atomic state. This is a serious limiting factor and must cause the spectrum to be much weaker than theoretically possible.

Rate of feed of the sample has an important effect on this step because it will control the amount of energy from the flame per unit weight of sample available to vaporize it and liberate free atoms. When feed rates are too high, the energy will be used in evaporating water droplets and few metal atoms will be liberated. Flame temperature is also very important because this, too, controls the efficiency of production of metals from solution by rapidly evaporating the water in the droplets.

When the metal is in an *organic solution*, the picture is quite different. Presumably it is combined with an organic molecule or it would not be in solution. When the solution is introduced into the flame, it not only evaporates, but also burns, insuring rapid vaporization of the sample.

The combined metal under these conditions is not so reluctant to volatilize. Also, the metal is combined to an organic addend which itself is able to burn and leave the free metal atom. It is probable that this process is rapid compared to the aqueous solution, and should result in a much more efficient production of metal atoms.

Further, it is possible that in the instance of release from the organic addend, the valence electrons of the metal are in an excited state, and at least some of them would return to the ground state with radiation of quantized energy—*i.e.*, exhibit the metal emission spectrum.

A schematic representation of the process of obtaining flame emission spectra is as follows:

Aqueous solution

Ions in water droplets	→	Evaporate to hydrated metal residue	→	Dehydrate and reduce to atoms or other active species (oxide bands)	→	Excitation	→	Emission
					→	Absorption		

Organic solution

Metal in organic solution	→	Solvent burns leaving organo-metallic compound	→	Organic addend burns, leaving atoms	→	Excitation	→	Emission
					→	Absorption		

Numerically this can be represented as follows: Suppose we have a solution containing 10,000 metal-containing molecules per unit volume.

PREVIOUS MECHANISM

Solution	*No. atoms in solution*		*No. metal atoms obtained in flame*		*No. excited atoms*		*Signal strength*
Aqueous	10,000 metal containing molecules	→	1,000	→	10 excited atoms	→	Emission E_1
				→	990 ground state atoms	→	Absorption A_1
Organic	10,000	→	1,000	→	50 excited atoms	→	Emission $(5 \cdot E_1)$
				→	950 ground state atoms	→	Absorption $\left(\frac{950}{990} A_1\right)$

PROPOSED MECHANISM

Solution		*No. atoms in solution*		*No. metal atoms obtained in flame*		*No. excited atoms*		*Signal strength*
Aqueous	→	10,000	→	1,000	→	10 excited atoms	→	Emission E_1
						990 ground state	→	Absorption A_1
Organic	→	10,000	→	5,000	→	50 excited atoms	→	Emission $(5 \cdot E_1)$
						4,950 ground state atoms	→	Absorption $\frac{4950}{990} A_1 = 5A_1$

The numbers used are not in any way to be interpreted as the actual numbers involved, merely the ratios of the numbers involved.

These different mechanisms would result in the organic solvent producing a greater population of atoms, excited or otherwise, from a solution of given concentration. This would result in more internal emission and absorption from organic solutions than from aqueous solution.

Although these suggested mechanisms are not completely proven, further support for the proposal is found in the fact that carbon tetrachloride, when used as a solvent, enhances absorption and emission signals. This compound in many ways acts like water in a flame. It does not burn, but can decompose, thereby reducing flame temperature. However, in all other respects, it acts as an organic compound. It is clear from the results that its function as an organic compound is more important than the effect it has on flame temperature.

It has also been observed in work at these laboratories that frequently more intense spectra are obtained from organic solvents and oxy-hydrogen flames (3500°K) than from aqueous solvents and oxy-cyanogen flames (4000-4500°K). In this case, although the temperature of the latter system is higher than the former, the use of an organic solvent more than offsets the effect of a lower temperature.

This again illustrates that the type of solvent used exercise more control over the intensity of the emitted spectrum from flames than the temperature of the flame.

GENERAL CONCLUSIONS

There is no doubt that flame temperature is a major factor in controlling the intensity of emission spectra from metals in flame photometry. However, it must be conceded that it may not be the only controlling factor. It is proposed that the combustion pattern and the efficiency of production of the emitting species play an equally and sometimes more important part in determining emission intensity.

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SUMMARY

It has been observed that organic solvents enhance the signal emitted by metals in flame photometry. They also increase the degree of absorption by metals in atomic absorption spectroscopy. It has been stated that this enhancement is caused by an increase in flame temperature. However, this temperature increase will not normally produce an increase in absorption. An alternate mechanism based on the combustion pattern of aqueous and organic solvents is proposed. The mechanism suggests that with organic solvents the emitting or absorbing species are produced more efficiently in the flame.

RÉSUMÉ

L'auteur a effectué une étude sur l'influence des solvants organiques et aqueux lors de spectrophotométrie par émission (spectres de flamme) et par absorption atomique.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss des Lösungsmittels auf die Emission der Metalle bei der Flammenphotometrie. Organische Lösungsmittel ergeben eine höhere Intensität des Emissionsspektrums.

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SEPARATION OF MICROGRAM AMOUNTS OF COBALT IN NICKEL METAL BY TRIBUTYL PHOSPHATE

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A determination of microgram amounts of cobalt is often needed, particularly in nickel used for the production of radio-cobalt. Methods used for separation and determination of cobalt have recently been reviewed by Bagshawe[1] and Andrew and Gentry[2]. None of the methods reviewed is satisfactory for the determination of below 100 p.p.m. of cobalt.

Recently Kraus and Moore[3] have studied the ion-exchange separation of nickel and cobalt at various hydrochloric acid concentrations. Mellish and Payne[4] have reported 80% recovery of radioactive cobalt from irradiated nickel on elution. Iida and Hirano[5] have used Amberlite IRA-400 resin to separate nickel from cobalt and have applied the method to the analysis of cobalt in mond nickel (cobalt about 8 p.p.m.).

Preliminary trials showed that tributyl phosphate (TBP) extracts cobalt selectively at high hydrochloric acid concentration; the small amount of residual nickel does not interfere seriously in the subsequent determination with nitroso-R salt. In this paper a method is described for separating major amounts of nickel by extraction with TBP followed by determination of cobalt with nitroso-R salt.

Reagents

40% Tributyl phosphate in mineral turpentine: TBP was shaken with a 5% solution of sodium carbonate to remove mono- and dibutyl phosphate, washed several times with water and finally diluted with mineral turpentine to give a 40% TBP solution. This was equilibrated by shaking with concentrated HCl ($d = 1.16$) before use.

Standard nickel solution: 101.225 g of $NiCl_2 \cdot 6H_2O$ (BDH AnalaR grade) was dissolved in 100 ml of 10% HCl by volume and finally made to 250 ml (10 ml = 1 g nickel).

Standard cobalt solution: 1 g cobalt metal (E. Merck) was dissolved in 20 ml of concentrated HNO_3 and made to 1 l. Aliquots were tested for purity by the α-nitroso-β-naphthol method (ASTM); the metal was over 97.0% pure. A final dilution was made to give a concentration of 1 ml = 10 μg of cobalt.

Nitroso-R-salt: 0.75% aqueous solution was prepared from B.D.H. reagent.

Sodium acetate: 50 g of sodium acetate trihydrate (E. Merck pure) was dissolved in water and diluted to 100 ml.

Distribution coefficient of microgram amounts of cobalt in HCl and TBP

Table I gives the results of a single extraction with 40 ml of 40% TBP in mineral turpentine from 20 ml of aqueous phase varying from 1 to 10.5 *N* in HCl concentration and containing 50 µg of cobalt.

TABLE I

DISTRIBUTION OF COBALT BETWEEN 1–10.5 *N* HCl AND 40% TBP DILUTED WITH MINERAL TURPENTINE

No.	*HCl* *N*	*Cobalt taken in 20 ml of aqueous phase µg*	*Cobalt extracted in 40 ml of 40% TBP µg*	*Distribution coefficient Co/Cw*
1	1.0	50	1.0	0.01
2	3.0	50	1.0	0.01
3	5.0	50	2.0	0.02
4	6.0	50	6.0	0.07
5	8.0	50	13.0	0.18
6	10.5 (conc.) (d = 1.16)	50	29.0	0.69

The results show that the extractibility of cobalt in 40% TBP increases with increasing concentrations of hydrochloric acid and reaches 58% when the hydrochloric acid concentration is 10.5 *N*.

50 µg of cobalt in 20 ml of 10.5 *N* HCl were extracted with four successive 40-ml portions of 40% TBP and then back-extracted four times with 40 ml of water. The combined back-extractions were tested with nitroso-R salt and showed over 95% recovery of cobalt.

With 1 g of nickel and 50 µg of cobalt under similar conditions, due care being taken to avoid any mechanical carry over, a small amount of nickel was also extracted with TBP, the amount varying from 10–12 mg.

Extraction of cobalt in TBP improved when 12 *N* HCl was used and simultaneously the nickel content of the extract decreased. However, since fuming HCl was not considered suitable for routine work and since 10–12 mg of nickel does not seriously affect the estimation of cobalt with nitroso-R salt, further experiments were carried out with 10.5 *N* HCl only.

PROCEDURE

10 ml of nickel solution (equivalent to 1 g nickel) was evaporated to dryness in a 100-ml beaker. (In case of nickel metal, 1 g of the metal was dissolved in concentrated HCl and evaporated to dryness). The contents were dissolved in 10 ml of conc. HCl (d = 1.16, 10.5 *N*). The solution was cooled and transferred to a 100-ml separatory funnel. The beaker was rinsed with 10 ml of concentrated HCl. The total volume of the qaueous phase was 20 ml. 40 ml of 40% TBP was added and the contents were shaken for two minutes. The phases were allowed to separate and the organic phase was transferred to another 250-ml separatory funnel. The extraction was repeated three more times, the organic phase being collected in the second funnel. The cobalt in the organic phase was stripped with 4 portions each of 40 ml water. The solution was evaporated to dryness and the organic matter was removed by repeated evaporation

with nitric acid and few drops of hydrogen peroxide. The solution was finally transferred to a 50-ml beaker and evaporated to dryness on a water bath. The residue was taken up in 10 ml of water. Cobalt was estimated in the solution spectrophotometrically with nitroso-R-salt.

Determination of cobalt

To the final 10 ml water extract of the cobalt solution, 5 ml of sodium acetate and 4 ml of nitroso-R-salt solution were added. The beaker was covered with a watch glass and was heated to boiling. This temperature was maintained for one minute to develop the colour of the cobalt complex fully. 5 ml of nitric acid (1 : 2) was then added and the solution was again boiled for about 2 min. The solution was cooled, transferred to a 50-ml volumetric flask and made up to the mark. The optical density was measured on Beckman DU spectrophotometer, using 1-cm pyrex cell at 520 mμ against a reagent blank.

The recoveries were calculated from a standard graph obtained with 0–50 μg of cobalt in a 50-ml volume.

Since 10–12 mg of nickel was found to be associated with cobalt it was necessary to find out its contribution to the optical density in the colour measurement. For this 4 lots of 1 g of cobalt-free nickel were taken through the whole procedure. The contribution of nickel to the optical density varied between 0.006 and 0.010; the average value of 0.008 was deducted in all subsequent cobalt estimations. The method described for the determination of cobalt with nitroso-R-salt is essentially the same as that given by ASTM[6] except that the amount of nitroso-R-salt was doubled. According to SANDELL[7] about 16 mg of the reagent are required to form a coloured complex with cobalt in presence of about 12 mg of nickel and 60 μg of cobalt required 2 mg of the reagent. Therefore, the quantity of reagent added in the ASTM method (15 mg) was just sufficient and gave quantitative results up to a maximum of 10 μg of cobalt. According to YOUNG[8] the addition of nitroso-R-salt up to 30 mg does not show any appreciable change in the optical density. Thus the quantity of reagent used in this work was appropriate in the range of estimation studied; *i.e.* 0–50 p.p.m. of cobalt in 1-g samples of nickel.

In order to estimate the efficiency of the method described, the method of standard

TABLE II

RECOVERIES OF 0–50 μg OF COBALT ADDED TO 1 g NICKEL

No.	*Amount of nickel taken* g	*Cobalt added in* μg	*Cobalt obtained in* μg	% *recovery of added cobalt*	
				Obtained	*Calculated from partition data*
1	1.00	—	6.0[a]	—	—
2	1.00	10.0	15.6	96.0	96.88
3	1.00	20.0	25.0	95.0	96.88
4	1.00	30.0	34.8	96.0	96.88
5	1.00	40.0	44.0	95.0	96.88
6	1.00	50.0	53.5	95.0	96.88

[a] Nickel used contained 6 p.p.m. of cobalt and has been corrected for.

addition of cobalt was followed. To 1 g nickel in the form of chloride, 10 to 50 µg of cobalt was added and the procedure described was used. The nickel solution taken as basis for testing recoveries gave an optical density of 0.04 (6 p.p.m. of cobalt). This has been corrected for in evaluating the results which are given in Table II.

The results show that the method can be successfully applied for the determination of microgram amounts of cobalt in nickel metal.

SUMMARY

A method has been developed for the separation of µg amounts of cobalt in nickel with 40% tributyl phosphate in 10.5 *N* hydrochloric acid; a nitroso-R salt finish is used and even 5 µg of cobalt in nickel can be estimated.

RÉSUMÉ

Une méthode est proposée pour la séparation du cobalt d'avec le nickel, par extraction au moyen de phosphate de tributyle. Le cobalt est finalement dosé par le sel de nitroso-R.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Trennung kleiner Mengen Kobalt von Nickel durch Extraktion mit Tributylphosphat. Die Bestimmung des Kobalts erfolgt mit Nitroso-R-Salz.

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DETERMINATION OF ARSENIC IN BIOLOGICAL MATERIAL BY THE ARSENIC MIRROR TEST

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The classical procedure for the isolation and identification of arsenic is the arsenic mirror test, which was introduced by MARSH AND BERZELIUS*. Although it is often employed for identifications the arsenic mirror has been used only occasionally for quantitative purposes[3,4]. By combining the qualitative and quantitative tests, material and time can be saved. RAMBERG[5] dissolved the mirror in iodine solution, whereas GANGL AND VÁZQUEZ SÁNCHEZ[6] used iodine monochloride; both determined the arsenic iodometrically. MORRIS AND CALVERY[7] and JANKE *et al.*[8] dissolved the mirror in nitric acid and determined the arsenic as molybdenum blue. JACOBS AND NAGLER[9] absorbed arsine, without preparing an arsenic mirror, in a hypobromite solution and also determined the arsenic as molybdenum blue.

In this paper, a method for identification and quantitative determination of arsenic for forensic purposes has been worked out, which is based on the isolation of the element as an arsenic mirror. The arsenic was determined by a modification of JACOBS AND NAGLER's method, and the identification was confirmed by paper chromatography and infra-red spectrophotometry.

APPARATUS AND REAGENTS

Digestion apparatus according to KLEIN[10], as described in a previous communication[11].

Mirror tubes of Jena Supremax-glass with a wide part (length about 10 cm, outer diam. 8–9 mm, thickness 1 mm) and a narrow part (length 10 cm, outer diam. 2 mm).

Marsh apparatus with a 250–300-ml Erlenmeyer flask with a standard socket, an inlet tube for hydrogen, reaching nearly to the bottom of the flask, and a graduated dropping funnel for the addition of the solutions. Escaping gases pass through a drying tube containing granulated calcium chloride and the mirror tube, which is positioned in a vertical cylinder formed by a sheet of asbestos board. A small Meker burner beneath the cylinder strongly heats a limited section of the tube. This type of apparatus did not give a quantitative yield. Marsh apparatus which yield arsenic quantitatively in the absence of heavy metals have been constructed[6,7]. However, as heavy metals are nearly always present in biological samples, quantitative yields are not to be expected even with an apparatus of this kind. Therefore it was considered simplest to use the traditional Marsh apparatus described above.

Arsenic standard, 1 mg As/ml. Arsenic trioxide (660 mg) was dissolved in sodium hydroxide (20 ml of 5 *N*). The solution was transferred to a 500-ml volumetric flask and, after the addition of sulphuric acid (40 ml of 5 *N*), made up to volume with water.

Diluted arsenic standard, 20 µg As/ml. The arsenic standard was diluted with water (10 : 500). The solution was stable for a week.

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* It is often called the Marsh-Liebig test, which is incorrect since BERZELIUS[1] made the same proposals as LIEBIG[2] four months earlier.

Zinc. 1. Granulated zinc for forensic purposes. E. Merck, Darmstadt. 2. Zinc, special for Gutzeit test, AnalaR reagent, British Drug Houses, London. The latter consists of granules with a large surface.

Mohr's salt. Ferrous ammonium sulphate hexahydrate (7 g) was dissolved in water (100 ml). The solution was stable for a week.

Bromine water. Saturated.

Hypobromite solution. Water (50 ml), sodium hydroxide (5 *N*, 2 ml) and saturated bromine water (30 ml) were mixed.

Molybdate solution. Ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$, (5.00 g) was dissolved in water and transferred to a 100-ml volumetric flask. A mixture of water (25 ml) and concentrated sulphuric acid (15 ml) was added. After cooling the solution was made up to volume with water.

Hydrazine sulphate solution. Hydrazine sulphate, $N_2H_4 \cdot H_2SO_4$, (2.00 g) was dissolved in water (100 ml).

DETERMINATION OF ARSENIC

Digestion and pretreatment

The recommendations of ANDREWS[12] and STRINGER[13] concerning digestion and pretreatment of the samples were generally followed. Samples with a high mineral content would require isolation of arsenic by distillation[13]. The destruction of organic matter was performed by digestion with nitric and sulphuric acids. For a detailed description reference is made to WANNTORP[11] and DYFVERMAN[14].

The wet oxidation was carried out as previously described for thallium[14], heating with ammonium sulphate being included. When the digestion flask had cooled somewhat, hydrazine sulphate (0.5 g) was added through a wide glass tube. The flask, with its central neck open and side neck stoppered, was heated with a small flame whereupon the contents darkened. The flame was gradually raised and the contents again became clear. The flame was regulated so that the sulphuric acid refluxed half-way up the flask walls, and heating was continued for 5 min. After cooling the flask was stoppered. (Work could be interrupted at this point).

Marsh–Berzelius' test

When the sample contained more than about 0.1 mg of arsenic, it was convenient to dilute the contents of the digestion flask to 50 ml with water and take an aliquot. Otherwise, the contents were diluted with water (50 ml) and allowed to cool.

Into the Marsh flask was weighed zinc (40 g); about 20 g of each type (see above). The rate of hydrogen generation was influenced by the relative amounts of the two types of zinc. The Marsh apparatus was assembled and hydrogen, which had been passed through a washing bottle containing water, was allowed to stream through for 5–10 min. A test-tube was filled under water with the escaping hydrogen, and then the gas in the tube was ignited to check that the air had been expelled. The gas was then ignited at the tip of the mirror tube, and the hydrogen stream was regulated so that a small flame (2–3 mm) burned continually. A small Meker burner was lit under the wide part of the mirror tube close to the taper. The Mohr's salt (10 drops to activate the zinc) and sulphuric acid (25 ml of 5 *N*) solutions were then added through the dropping funnel. (When the stopcock is closed, a few drops of the solution should be left in the funnel). The apparatus was allowed to run for 30 min, after which time no dark deposit should be visible in the mirror tube.

The diluted contents of the digestion flask were slowly run into the Marsh flask. The flask was rinsed with sulphuric acid (25 ml of 5 *N*), into the Marsh flask. The generation of hydrogen was at first so rapid that the gas from the cylinder could be turned off; later, additional hydrogen was again needed. It was important not to let the generation of hydrogen in the flask become too lively, because this reduced the yield of arsenic. The evolution could be moderated if necessary by placing the flask in a dish through which cold water circulated. The apparatus, with the sample added, was allowed to run for one hour. The burner was then turned off and the hydrogen supply stopped. The mirror tube, when cold, was closed at both ends. The final determination should follow as soon as possible.

Determination

With JACOBS AND NAGLER's method[9] it proved inconvenient to use a half-saturated solution of hydrazine sulphate as a reducing agent, because its solubility is strongly temperature dependent. The composition of the hydrazine sulphate solution was therefore changed (see above), and the proper amount of this solution was experimentally determined to be 1 ml. With 0.9 ml the colour developed too slowly, and with 1.2 ml the maximal colour intensity was less. The time for the development of the molybdenum blue complex was increased from 30 min to 2 h. After this time the colour still deepened, but only slowly. A variation of ± 10 min changed the reading by about 0.5%. The temperature in our laboratory was about 20°.

The mirror tube was provided with a rubber bulb at the thick end. The tip of the mirror tube was dipped into hypobromite solution (3.00 ml) in a test tube, and the solution was sucked up and down. The arsenic mirror dissolved within a minute. The inside of the tube was kept in contact with the solution for a further 5 min. The solution was then transferred to a 25-ml volumetric flask and the test and mirror tubes were rinsed with water (3 4 ml). The blank was prepared in another volumetric flask (25 ml) with hypobromite solution (3.00 ml) and water (12 ml).

To each of the flasks was added sulphuric acid (5.0 ml of 2 *N*) followed by molybdate solution (1.00 ml) and hydrazine sulphate solution (1.00 ml); the solution was mixed thoroughly by swirling between each addition.

The solutions were diluted to the marks with water, the contents mixed and the stoppers removed. The time was counted from this point. The solutions formed gas bubbles and the flasks were therefore placed in a desiccator under moderate vacuum (protected from strong daylight). After 2 h ± 10 min the absorbance of the sample solution was measured in a spectrophotometer against the blank at 830 mμ in 1-cm cells. If the solutions still formed bubbles, these were removed with the help of thin plastic rods.

Calculation: The amount of arsenic in the whole sample (or in an aliquot, see below), in μg was $k_{25} \cdot A_{830}$, where k_{25} was obtained from a standard curve and A_{830} was the absorbance found. The values obtained had to be corrected for losses in the Marsh apparatus (see under Yields).

Standard curve

To five volumetric flasks (25 ml) were added hypobromite solution (3.00 ml), diluted arsenic standard (0; 1; 2; 3 and 4 ml), and water (12; 11; 10; 9 and 8 ml). The procedure was then as described under "determination". The arsenic-containing solutions were measured against the blank at 830 mμ. The A_{830}-values were plotted against the amount of arsenic in μg, a straight line relationship being obtained (Fig. 1). The amount of arsenic, corresponding to $A_{830} = 1.000$, was denoted by k_{25}. A mean value of $k_{25} = 73.5$ was obtained.

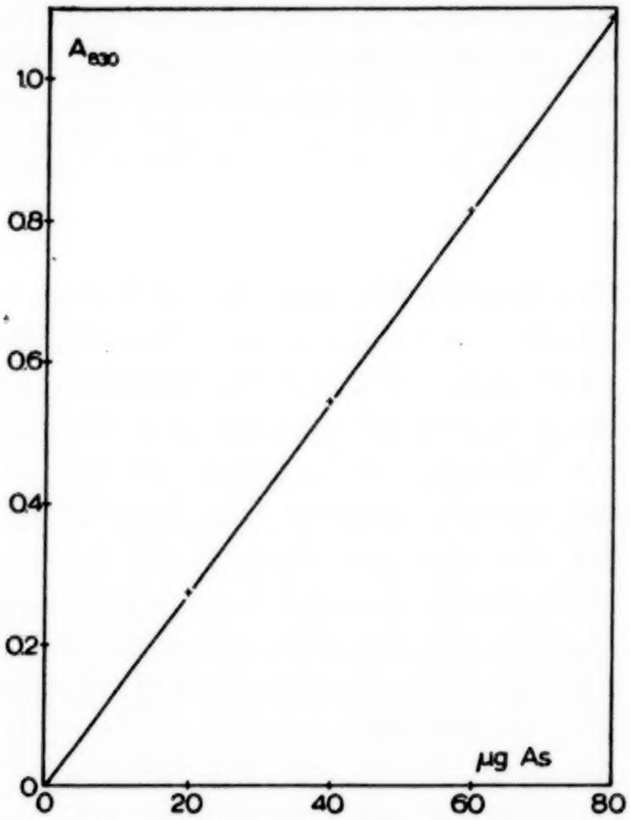

Fig. 1. Standard curve for arsenic.

More than 80 μg As

With experience the arsenic content of a mirror could be estimated visually. When the mirror contained more than about 80 μg of arsenic, it was dissolved in hypobromite solution (3.00 ml) and the solution was diluted with water to 25 ml. An aliquot of this solution, 15 ml at most, was transferred to another 25-ml volumetric flask. An extra addition of hypobromite was made, bringing the total amount of hypobromite solution present to 3.00 ml. The solution was diluted with water to about 15 ml, and the determination was continued as described above.

Less than 15 μg As

For the smallest mirrors, with less than about 15 μg of arsenic, it was convenient to carry out the determination with 5-ml volumetric flasks, reducing the volume of all reagents by a factor of 5. The amount of arsenic in the whole sample in μg was then $k_5 \cdot A_{830}$, where $k_5 = k_{25}/5 \approx 14.7$.

Yields

As mentioned above the arsenic was not quantitatively deposited in the mirrors. The yields had therefore to be determined by the addition of known amounts of arsenic to tissue samples, which were then analysed. In Fig. 2 curves are presented which show the yields obtained after the addition of arsenic standard directly to the Marsh apparatus, and to 5-g and 25-g samples of muscle or liver. With the help of such curves the losses in the analytical procedure were corrected for.

At the lower limit of the determination, about 2 μg of arsenic, the yields were about 50%, and at the optimal amount, 25–75 μg, yields from 65 to 85% were obtained. With larger tissue samples (the amount of arsenic being kept constant) the yields became lower.

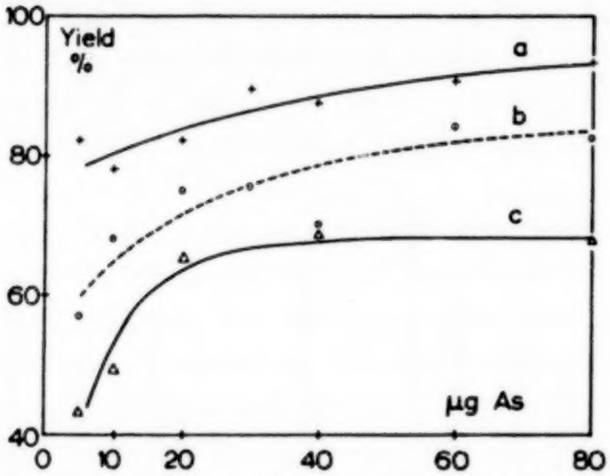

Fig. 2. Yield curves for arsenic. (a) Marsh apparatus only. (b) Human muscle (5 g, with arsenic added). (c) Human liver (25 g).

INTERFERENCES

Negative interferences

Many substances more or less impede the generation of arsine during the Marsh test and lower the yield of arsenic. To this category belong a number of heavy metals (Fe, Hg, Pt, Ag, Pd, Ni, Co, Cu), sulphur compounds where sulphur has a valency below 6, oxidising compounds such as nitric and nitrous acids and organic compounds[3]. After correct pretreatment of the sample only metals need be considered. Mercury interferes most seriously, because it entirely prevents the formation of arsine. If mercury is present, this metal has to be removed. The metals that normally occur in biological material, *e.g.* iron and copper, lower the yield to some extent (*cf.* Fig. 2).

Positive interferences

Positive interferences can be expected from substances that deposit in the mirror tube and cause the ultimate formation of molybdenum blue or of blue colours. Mirror deposits have been obtained from compounds of boron, carbon, silicon (valency < 4), phosphorus (valency < 5), antimony, bismuth, sulphur (valency < 6), selenium and tellurium[3]. In oxidised samples carbon should not be present. Bismuth can only be reduced to the hydride with difficulty. In the molybdenum blue method, blue colours can appear with arsenate, phosphate, silicate and germanate[15] and with tungstate, beryllium and titanium[16].

Experiments which were carried out with the addition of most of these substances are summarised in Table 1. In some cases relatively large deposits were obtained in the mirror tubes. These could usually be differentiated from arsenic mirrors by their appearance. Often small deposits were obtained which were very similar to small arsenic mirrors. The coatings usually lay nearer to the hot zone than the arsenic mirror, except that formed by phosphorus(III). In some experiments changes were noted in the Marsh flask: with germanium and bismuth brown or black and with

TABLE I

POSITIVE INTERFERENCES

Element added		*Compound added*	*Treatment*	*Deposit*			*Found "As" μg*
	mg			*Size*	*Colour*	*Solubility*	
—	—	—	L	small	brownish	e.s.	1.7
Be(II)	100	$Be(NO_3)_2 \cdot 3H_2O$	M	none	—	—	0.3
Be(II)	100	$Be(NO_3)_2 \cdot 3H_2O$	H	rather small	brown, disappeared	—	0.5
B(III)	44	H_3BO_3	M	very small	brown shadow	e.s.	0.5
Si(IV)	105	$Na_2SiO_3 \sim 8H_2O$	M	very small	brown, disappeared	—	0.2
Si(IV)	26	$Na_2SiO_3 \sim 8H_2O$	H	very small	brown, disappearing	—	0.6
Ge(IV)	162	$GeCl_4$	M	very large	gray and black, brilliant	e.s.	0.4
Ge(IV)	150	Germanic acid, ppt	H	large	grayish black, brilliant; brown	s.	1.2
Ti(IV)	60	TiO_2	H	very small	brown	e.s.	0.8
P(III)	490	H_3PO_3	M	rather large	yellow, narrow blue zones	s.	57
P(III)	246	H_3PO_3	L	small	white haze	e.s.	2.4
P(V)	460	H_3PO_4	M	small	gray	s.	0.5
P(V)	920	H_3PO_4	H	rather small	gray to grayish brown	sl.s.	2.3
P(V)	650	H_3PO_4	L	very small	brown bands	e.s.	3.0
P(V)	975	$Na_2HPO_4 \cdot 2H_2O$	H	small	gray to dark brown	e.s.	1.7
Sb(III)	0.5	$SbCl_3$	M	large	grayish black, sl. brilliant	i.	0.2
Bi(III)	60	$Bi_2(SO_4)_3$	H	none	—	—	1.5
V(V)	170	V_2O_5	H	very small	light brown	e.s.	0.6
Se(VI)	10	H_2SeO_4, 40%	M	medium	grayish black and red	e.s.	0.5
Te(VI)	10	$H_2TeO_4 \cdot 2H_2O$	M	none	—	—	—
W(VI)	140	$Na_2WO_4 \cdot 2H_2O$	H	small	brownish, faint blue zones	e.s.	1.2

The substances were added directly to the Marsh apparatus (M), first heated with concentrated sulphuric acid and hydrazine sulphate (H), or added to 25 g of human liver and analysed in the usual manner (L). e. = easily, sl. = slightly, s. = soluble, i. = insoluble, ppt. = precipitate.

tungstate blue precipitates were formed, and with tellurium a black contour formed on the glass at the surface of the solution.

The coatings are briefly described in the table, but it may be added that the antimony mirror, which may be mistaken for an arsenic mirror, is mainly gray to black with weak brilliance, while the arsenic mirror is brown to black. Arsenic mirrors from more than 50 μg are very brilliant. Silicon-containing deposits practically disappeared within a few hours. Germanium gave a characteristic mirror, close to and partly surrounding the hottest zone. Most of these "false" coatings easily dissolved in hypobromite solution. Antimony was an exception, which may be of use for the analysis of antimony.

The deposits were analysed as for arsenic and the results are shown in Table I. Most of the substances added yielded only small final readings, which had no toxicological significance. Only in one case, when phosphorous acid was added directly to the Marsh flask, was a large reading obtained. When phosphorous acid was added to liver and then analysed in the usual manner, the reading was small, considering that the value of the blank determination for the liver sample, 1.7 μg of arsenic, had to be subtracted. With phosphorus (0.5–1 g) in the form of phosphoric acid or soluble phosphate, values corresponding to about 1–2 μg of arsenic were obtained; these have no notable toxicological significance.

IDENTIFICATION OF ARSENIC

A brown or black, possibly shining, mirror deposit along with a positive reading in the above colorimetric determination can be considered as proof of the presence of arsenic. However, confirmation is desirable, and the spectra (visible and infra-red) of the arseno–molybdenum-blue and analogous complexes have therefore been measured. A procedure for the chromatographic identification of arsenic has also been worked out.

Absorption spectra

(*a*) ***Visible and near infra-red regions.*** To 25-ml volumetric flasks were introduced 80 μg As (diluted arsenic standard, 4 ml), 40 μg P (phosphate standard, 10 μg P/ml,

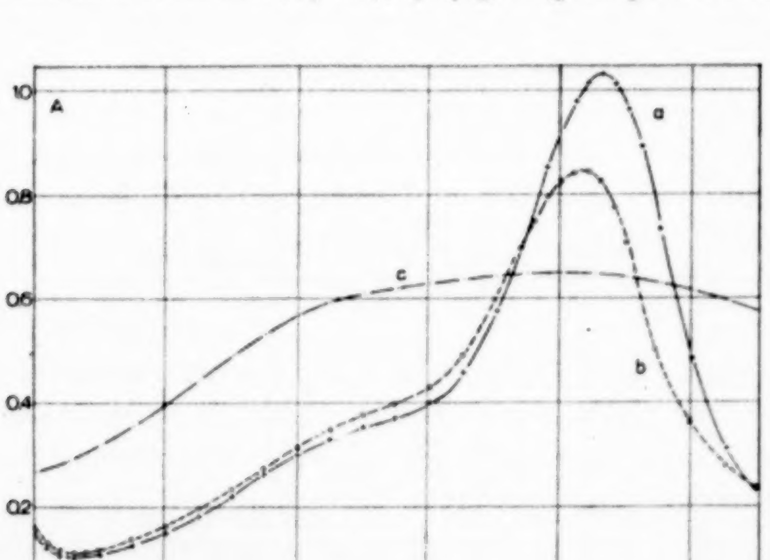

Fig. 3. Absorption spectra of heteropoly blue complexes with (a) arsenate, (b) phosphate, and (c) tungstate in the visible and near infra-red. *A* = absorbance.

4 ml) and 1.75 mg W (sodium tungstate solution, 10 mg W/ml, 175 μl). Heteropoly molybdenum blue complexes were formed as described above. The absorbances were measured against water (Fig. 3).

The absorption curves for arsenate and phosphate were very similar, but the maxima at about 830 and 815 mμ respectively were clearly separated. The tungstate curve was flat with an indistinct maximum at about 800 mμ. With beryllium nitrate, sodium silicate, germanium, and titanium trichloride no colours developed.

(*b*) *Infra-red spectra.* Water solutions (volume 25 ml) prepared in the same manner as above (see (a)) were shaken with ethyl acetate (10 ml) for 30 sec. The water phases were discarded and the organic phases were dried over sodium chloride and filtered into glass dishes (diam. about 5 and height 3 cm), containing 0.4 g of potassium bromide (ignited and kept over phosphorus pentoxide). The ethyl acetate solutions were evaporated overnight in the dark at 30–35°. The bromide was then pulverised very carefully and dried in vacuo over phosphorus pentoxide for two days. Bromide discs were pressed in the usual manner and kept over phosphorus pentoxide. Spectra of the discs were recorded *versus* a disc of pure potassium bromide in the Hilger double beam infra-red spectrophotometer H 800.

In the experiments with arsenate and phosphate, the blue colours were nearly completely extracted by ethyl acetate, but with W, Be, Si, Ge and Ti the ethyl acetate extracts were colourless and did not apparently contain any heteropoly-blue complexes. Arsenic could be identified by an absorption maximum at a wave number (ν) of 980 cm^{-1}. As little as 25 μg of arsenic could be identified in the absence of phosphorus, which had a large peak at 962 cm^{-1}. 25 μg phosphorus could easily be identified by peaks at 962 and 1065 cm^{-1}, the latter being very characteristic. Other maxima appeared with arsenic and phosphorus, but these were less useful for identification. The spectra for arsenic, phosphorus and a blank from 700 to 1800 cm^{-1} are reproduced in Fig. 4. Characteristic absorption bands were not recorded between 1800 and 4000 cm^{-1}. The heights of the maxima, calculated as absorbances, increased with increased amount of the substances, but more rapidly than would be expected from Beer's law.

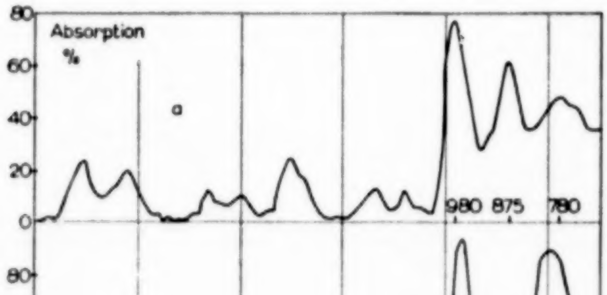

Fig. 4. Infra-red absorption curves for heteropoly blue complexes with (a) arsenate (100 μg As) and (b) phosphate (50 μg P). (c) Blank.

To obtain clear absorption bands with beryllium and tungstate, larger amounts had to be taken. With beryllium (2.5–5 mg) in three experiments a peak was obtained at 1388 cm^{-1}, but otherwise the spectrum was not reproducible. With tungsten (1.25–2.5 mg) reproducible spectra were not obtained in three experiments. With silicon (5 mg), germanium (2 mg) and titanium (5 mg) the spectra corresponded to that of the blank.

Chromatography

Procedure. The mirror was dissolved in half-saturated bromine water (0.5 ml). The solution was evaporated to about half its volume by heating in a small tube on a steam bath, the vapour being removed by suction. The tube was heated and swirled to dissolve deposits on the walls. The solution was transferred using the mirror tube to a chromatographic paper (Whatman No. 54, cut lengthwise and serrated on the bottom edge). Standard solutions of arsenate and phosphate (10–20 μl of $M/75$) were also placed on the paper.

A chromatographic technique which has been used for the separation of phosphate esters[17], was employed, the only changes being that the papers were not washed and the time of development was shortened from 20 to 16 h. The solvent contained *n*-butanol, trichloroacetic acid, ethanol and water. After drying, the chromatogram was dipped in a molybdate reagent, redried and sprayed with a solution of ascorbic acid. The substances appeared as blue spots. The positions of the spots are given in relation to orthophosphate, as R_P-values[17].

Results

The main portion of the arsenic from a mirror appeared as an arsenate spot; 10 μg of arsenic could easily be identified by this spot. In most experiments a faint spot also appeared closer to the starting position. This spot has not yet been identified.

Since the spots consist of molybdenum blue complexes tests were carried out with the substances mentioned above, which were expected to produce molybdenum blue colours. With relatively large amounts of tungstate (0.2 mg W) and titanium trichloride (1 mg Ti) indistinct spots were obtained (at $R_P = 0.85$ and a tail respectively). Attempts to produce chromatographic spots from beryllium, silicate and germanate under the given conditions failed. Solutions of pyrophosphate, phosphite and arsenite were also chromatographed. To make the arsenite spot emerge rapidly, the chromatogram had to be sprayed with diluted bromine water (1 + 10) and then dried before treatment with the molybdate reagent. The following R_P-values were obtained: Unknown arsenic spot – 0.34; pyrophosphate ($Na_4P_2O_7$) – 0.43; orthophosphate (K_2HPO_4) – 1.00; arsenite (As_2O_3 dissolved in NH_4OH) – 1.03; arsenate (Na_2HAsO_4) – 1.18; phosphite (H_3PO_3) – 1.32.

Acidification of an arsenate solution (1 ml of $M/15$ Na_2HAsO_4) with sulphuric acid (0.3 ml of 0.5 N) followed by chromatography gave, along with the arsenate spot, a large spot in the position of the previously found unknown arsenic spot. This spot may consist of a polymerized form of arsenic acid, although polymerized arsenates are reported to be unstable in aqueous solution[18].

SUMMARY

A method based upon Marsh–Berzelius' arsenic mirror test has been developed for the determination of arsenic in biological material. The arsenic mirror is dissolved in a hypobromite solution and the arsenic is determined colorimetrically by a heteropoly blue method. As little as 2 μg of arsenic in a 25-g sample of tissue can be determined. Mercury inhibits the generation of arsine; in doubtful cases a mercury determination[11] is carried out. Phosphoric acid and soluble phosphates (0.5–1 g P) caused weak positive interferences, equivalent to 1–2 μg As. Other positive interferences were not found. The arsenic obtained in the mirror was also identified by the absorption curves of its heteropoly blue complex in the visible and infra-red regions as well as by paper chromatography.

RÉSUMÉ

Les auteurs proposent une méthode pour le microdosage de l'arsenic dans des substances biologiques. On applique la méthode de Marsh–Berzélius; le miroir obtenu est dissous dans une solution d'hypobromite. L'arsenic est dosé finalement par colorimétrie par une méthode au bleu de molybdène.

ZUSAMMENFASSUNG

Beschreibung einer Mikromethode zur Bestimmung von Arsen in biologischen Substanzen nach der Methode von Marsh–Berzelius. Der erhaltene Arsenspiegel wird in Hypobromit gelöst und colorimetrisch bestimmt.

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Short Communications

Observations about certain complexing agents and their nomenclature

In 1958, one of us (F.B.) was charged by the Spanish–American Committee of Standardization (*Comisión Iberoamericana de Normalizaciones, CIN*) to organize a committee to write a statement on the analytical applications of ethylenediaminetetraacetic acid (EDTA) and related compounds which were known as *complexones*. The committee consisted initially of three of us (F.B., J.B. and A.P.) and submitted a report to CIN; the report was also submitted to the VIIth Latin American Meeting of Chemistry which was held in Mexico in March–April, 1959. This report (ponencia 4) dealt with the nomenclature of EDTA and related compounds and their analytical applications.

In this report[1] the necessity of establishing a condensed nomenclature and of introducing a new term to distinguish compounds analogous to EDTA was emphasized, because the term *complexone* had been claimed as an international trademark[2]. We recommended that the proposal of REILLEY[3] to designate polyaminopolycarboxylic acids and polyamines which are analytically useful by the term *chelons* should be adopted; the equivalent Spanish term would be *quelones*. These names have been used in almost every American or Spanish paper on these reagents since that time.

We were therefore very surprised to read the recent report of the *Committee of the Analytical Chemistry Section of IUPAC*[4-6] in which it was suggested that the polyaminopolycarboxylic acids forming anionic complexes should be designated as *complexans*; the Spanish equivalent is given as *complexanas*[5] or *complejantes*[6].

We believe that this proposal is a mistake because of its lack of logic, its ambiguity and its analogy with the international trademark. Moreover, *complejante* is quite wrong, for it actually means any type of reagent which forms complexes. The ambiguity of the term is also shown by the different translations into Spanish[5,6].

We agree that titration processes in which any type of complexing agent is used should be called *complexometric titrations* (valoraciones complexométricas o complejométricas). We also think it is correct to designate titrations in which a chelate-forming reagent is used as *chelatometric titrations* (to be grouped along with the analogous methods of argentometric or mercurimetric titrations in which silver or mercury complexes are formed).

However, chelatometric titrations should be further subdivided into, *e.g. chelometric titrations* (valoraciones quelométricas) based on the use of chelons as reagents, *oxinometric titrations, dithizonometric titrations, diethyldithiocarbamatometric titrations*, etc., based on the use of the respective reagents which form chelates with different cations. In this suggestion, we follow the old system of subdividing, *e.g.* redox titrations into permanganatometric, dichromatometric, cerimetric, iodometric, etc., titrations, according to the titrant used.

The proposed classification is given in the following table:

- *Complexometric titrations*
  - *Argentimetric titrations* (forming complexes with silver salts)
  - *Mercurimetric titrations* (forming complexes with mercury(II) salts)
  - *Chelatometric titrations* (titrations with a chelating agent)
    - *Chelometric titrations* (titrations with chelons)
      - Titrations with NTA
      - Titrations with EDTA
      - Titrations with DCTA
      - Titrations with EGTA
      - . . . .
      - . . . .
    - *Oxinometric titrations* (with oxine)
    - *Dithizonometric titrations* (with dithizone)
    - *Diethyldithiocarbamatometric titrations* (with DDTC)

In the classification there is no confusion of the type caused by terming titrations with polyaminopolycarboxylic acids as reagents, as *Komplexometrische titration* or *Chelatométrie*. These designations are wrong because of the more general meaning of the words *complex* and *chelate*. Thus *complexometric* or *chelatometric* titrations must embrace respectively any titration method which depends on complex or chelate formation.

Oxine, dithizone and diethyldithiocarbamate are already used as volumetric solutions, and it seems likely that other compounds of this type will shortly find applications as volumetric reagents. This will cause ambiguity unless a terminology exists to differentiate whether a chelatometric titration is done with polyaminopolycarboxylic acids or with some other complex-forming reagent.

If the term *complexans* is adopted as proposed by IUPAC, it will be difficult to differentiate clearly between different types of complexometric titrations (in which a complex of any kind is formed). Titrations based on the use of polyaminopolycarboxylic acids would then be named *complexanometric titrations*; the same ambiguity and confusion would be produced in Spanish between *valoraciones complexometricas* and *valoraciones complexanometricas* and in German between *Komplexometrische Titration* and *Komplexanometrische Titration.*

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Comment

Professor Bermejo and his colleagues follow the tentative recommendations of the Analytical Chemistry Section of IUPAC on the usage of the terms complexometric and chelatometric titrations, but they do not accept the term *complexan*, preferring Professor Reilley's suggestion of *chelon*.

I should like to comment on behalf of the Commission of Nomenclature (Chairman, Professor F. Burriel-Marti, Madrid) which still has the matter under consideration.

(*a*) The recommendation of *complexan* made by the IUPAC Section is tentative and was made during the recent IUPAC Conference in Munich in an attempt to stabilize the position until the Commission concerned could gather all the available information and reach a final recommendation. Any comments should preferably be sent to the Commission, for this mechanism permits much more rapid contact than is possible by publishing in a journal.

(*b*) The arguments against *complexan* also apply to *chelon*; chelon and chelate,

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chelometric and chelatometric, complexan and complex, complexanometric and complexometric lend themselves equally to confusion.

A purely personal opinion is that neither term is really necessary for a generic subdivision of chelatometric titrations. It would seem more logical and certainly more lucid to say, for example, titrimetric determination of calcium with EGTA (or whatever the titrant is) than to say either chelometric or complexanometric titration of calcium. Recommendations which result in such startling terms as *diethyldithiocarbamatometric titrations* should surely be avoided wherever possible.

Any comments on this matter will be valued by the Commission concerned.

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Alkali consumption in the dinitrophenylation of alpha amino acids*

Even though there appear statements in the literature as to the equivalents of base consumed per functional group of amino acid dinitrophenylated by FDNB (1-fluoro-2,4-dinitrobenzene), no definite data to document the quantitativeness of this procedure have been reported. Still such information is important for drawing a balance sheet when certain groups ($-NH_2$, $-OH$, etc.) in the protein or protein hydrolysate are dinitrophenylated. According to Levy[1], stirring an aqueous solution of the alpha amino acids with a slight excess of FDNB for 80 min at pH 9.0 and 40°, requires 1.54 equivalents alkali per NH_2 group, 0.77 equivalents for tyrosine OH and 0.19 equivalents for the imidazole ring of histidine (after due correction is made for the formation of dinitrophenol (0.44 μmol of OH^- ml^{-1} min^{-1}). According to Fraenkel-Conrat, Harris and Levy[2], at pH 8.0, it is found that 1.25 equivalents of alkali are consumed for each alpha NH_2 group, 1 equivalent for each tyrosine OH and each histidine imidazole and 2 equivalents for each epsilon NH_2 group of lysine reacting.

We would like to report here equivalents of base consumed at pH 9.0 and pH 7.8 when individual alpha amino acids and also certain peptides are dinitrophenylated. A mixture containing approximately 0.05 mmol of an amino acid in 30 ml of 0.1 *M* KCl was stirred at 40° and at the appropriate pH with approximately 2 ml of freshly distilled FDNB until the uptake of alkali per unit time became constant. From the table it appears that, at pH 9.0, particularly proline but also isoleucine and valine show higher base consumption than certain other amino acids such as methionine and serine. As expected there seems to be an increase in this consumption in the case of tyrosine, lysine, cystine and cysteine. For histidine, however, the value is lower than expected. Presence of peptides bonds reduces the amount of base consumed.

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TABLE I

ALKALI CONSUMPTION IN THE DINITROPHENYLATION OF ALPHA AMINO ACIDS*

	$\frac{\text{mequiv. NaOH}}{\text{mmol amino acid}}$	
	pH 9.0	*pH 7.8*
Alanine	1.74	0.85
Arginine	1.57	1.55
Aspartic acid	1.45	1.22
Cysteine	1.94	2.10
Cystine	2.56	3.15
Glutamic acid	1.67	0.91
Glycine	1.69	1.00
Histidine	1.50	2.00
Isoleucine	1.83	1.45
Leucine	1.63	1.05
Lysine	3.54	1.98
Methionine	1.53	1.63
Phenylalanine	1.41	1.54
Proline	2.04	2.58
Serine	1.45	1.55
Threonine	1.47	1.69
Tryptophan	1.66	1.85
Tyrosine	2.20	2.21
Valine	1.82	1.50
Glycyl-histidine	1.13	
Glycyl-leucine	1.17	
Glycyl-lysine	2.80	
Glycyl-tyrosine	1.81	

* Values are usually averages of three separate experiments. They are obtained by extrapolating to zero time the final slope of the curve: base consumed *versus* time.

The pH was maintained constant by intermittent additions of standard alkali. Duration of experiment was 90 min at pH 9.0, or 3–4 h at pH 7.8.

Decreasing the pH from 9 to 7.8 does not necessarily cause a decrease in milliequivalents of alkali consumed in the dinitrophenylation of all amino acids. Since regeneration of the parent amino acid from its corresponding DNP derivative is accomplished by alkaline hydrolysis, it is highly probable that a simultaneous but comparatively small hydrolytic reaction occurs whereby the DNP–amino acid formed is partially hydrolyzed and subsequently redinitrophenylated. This process could account for the lack of stoichiometry in the alkali consumed with the amount of DNP–amino acid formed and also for the variation in equivalents required by different amino acids.

Finally, it should be mentioned that the velocity constants for this reaction indicate a much more rapid uptake of FDNB at pH 9.0 if compared to those at pH 7.8.

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A COMPARISON OF THREE METHODS OF DETERMINING THE CONCENTRATION OF URANIUM IN SEA WATER

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INTRODUCTION

Earlier measurements of the concentration of uranium in sea water have been reviewed by KOCZY[1], and a number of results have also been tabulated by RONA, GILPATRICK AND JEFFREY[2]. It is clear from the results quoted in these papers that there are considerable variations in the uranium concentrations quoted by different observers, and that there is little agreement as to whether the uranium concentration varied with the locality and the depth at which the sample is taken. HERNEGGER AND KARLIK[3] for example, found a uranium concentration of 1.3 μg/l which was fairly independent of the depth at which the samples were taken, whilst both KOCZY[1] and NAKANISHI[4] found that the concentration increased up to a depth of 500 to 1,000 m after which it remained fairly constant. NAKANISHI's average value of 2.8 μg/l for depths below 500 m is, however, twice that obtained by KOCZY.

Large variations in the results of analyses of samples taken from different locations is understandable in the case of coastal waters, but is less so in the case of deep sea samples, and the table given by RONA, GILPATRICK AND JEFFREY shows that different observers have obtained results ranging from 0.7 to 3.5 μg/l for samples taken from near the surface in the same areas of the North Atlantic and North Pacific Oceans.

In view of the wide range of results which have been reported it would clearly be unsatisfactory to rely solely on any one analytical method in a new determination of uranium in sea water, and whilst a new polarographic method[5] for uranium in sea water was being developed in this laboratory the opportunity was taken to analyse a number of the sea water samples by the isotopic dilution (involving mass spectrometry) and the fluorimetric methods as well.

A second reason for doing this was to demonstrate that the differences in the results obtained by earlier workers were not primarily due to the different analytical techniques employed, *viz.*, D.C. polarography[6], fluorimetry[4], fission counting[7], and the isotopic dilution method[2].

An alternative explanation of some of the variations in the values which have been reported previously might be found in the fact that often no checks were made on the chemical yields in the extraction and concentration steps *in the actual analyses*. It was usually assumed that these recoveries were the same as those found in trial experiments with known amounts of uranium (although these recoveries were not always 100%). The experiments with radioactive tracers which are quoted in a previous paper[5] from this laboratory show, however, that it is extremely difficult to obtain recoveries of uranium from sea water reproducible to within 10% by the usual extraction procedures, so that the effect of variable chemical losses must be considered.

Some form of uranium tracer was used in all the methods described in this paper; ^{237}U for the methods using pulse polarography[5] and fluorimetry, and ^{235}U in the isotopic dilution method. In this way the effects of the variable chemical yields in the extraction steps were always known or eliminated. It may be observed that the mean value of $3.3_3 \pm 0.08$ μg/l for English Channel and Bay of Biscay waters obtained by the three methods is quite close to the value of 3.3_9 μg/l found for water from the North Atlantic and the Gulf of Mexico by RONA, GILPATRICK AND JEFFREY[2], who also used an isotopic dilution method.

In addition to giving a *consistent* value for the uranium content of sea water, the results permitted a comparison of the precision of the three methods to be carried out and indicated some possible sources of error in this determination. Details of the polarographic method[5] have already been given, and enough details of the isotopic dilution and fluorimetric methods are given in this paper to enable a proper comparison to be made.

THE ISOTOPIC DILUTION METHOD

The isotopic dilution method which was used involved the measurement of the $^{238}U/^{235}U$ ratio in sea water extracts after the ^{235}U tracer had been added to the original sea water. The tracer had the isotopic composition ^{234}U — 1.03%, ^{235}U — 93.41%, ^{236}U — 0.125%, ^{238}U — 5.44%, whereas natural uranium consists mainly of ^{238}U (99.3%). The concentration of the solution of this tracer was determined by calibration against a standard solution of natural uranium, so that in effect the natural uranium in sea water is compared against a standard solution of natural uranium and systematic errors which might be introduced by mass discrimination are eliminated.

In principle the measurement of the $^{238}U/^{235}U$ ratio makes the results obtained by the isotopic dilution procedure independent of the chemical yield; in practice if the contamination level from reagents, etc. is significant, small errors may be introduced if the chemical yield differs between a uranium determination and a blank determination. The uranium blanks in the method which is described were small, however, so this error was very small.

The determinations fell into two groups. Some preliminary measurements were made using a 6″ radius of curvature 60° sector mass spectrometer fitted with a simple D.C. amplifier detector. 1.5-l samples of sea water were used, the uranium being coprecipitated with aluminium phosphate and then purified by solvent extraction as the nitrate into ethyl acetate. In addition to being time consuming, this method gave rather high uranium blanks and its use was discontinued. The later determinations were made with a Metropolitan-Vickers M.S.5 mass spectrometer. This is a 12″ radius of curvature 90° sector instrument incorporating an electron multiplier detector, and its high sensitivity enabled much smaller samples of sea water to be analysed. The method which is described below involves the extraction of the uranium 8-hydroxyquinoline (oxine) complex into chloroform from 100-ml aliquots of sea water, and it is much shorter than the first method investigated.

Experimental method

Acidify the sea water immediately it is collected, with 2 ml of conc. nitric acid per l. Weigh about 2 g of ^{235}U tracer solution and 100 g of sea water into a polythene bottle, mix thoroughly, and allow to stand for 1 or more days to reach equilibrium. Then transfer the solution to a 250-ml separating funnel and add 1 ml of 20% w/v ammonium acetate and 1 ml of 0.1 *M* ethylenediaminetetraacetic acid disodium salt (EDTA). Adjust to between pH 6.5 and 7 by the addition of ammonium hydroxide using B.D.H. universal indicator, and then add 1 ml of a 6% w/v solution of oxine in alcohol. Extract the uranium complex with 3 ml of chloroform, add a further 1 ml of the oxine solution and make two more extractions with 3 ml and 2 ml of chloroform respectively. Evaporate the combined extracts to dryness in a platinum tray and ignite to remove any organic residue. Wash the tray with a small quantity of hot nitric acid and evaporate the washings to dryness on a circular glass plate or microscope slide. Dissolve the visible deposit in a small drop of water, and transfer to the sample filament of a mass spectrometer surface ionisation source. Then carry out an isotopic analysis.

Results for uranium in sea water

Table I shows the values obtained for the uranium content of coastal sea water using the co-precipitation of the uranium with aluminium phosphate from 1.5-l samples of sea water. Samples 'A' and 'B' were both taken at the same time and at the same place, but sample 'A' was stored in a 35-l polythene bottle, whilst sample 'B' was stored in a 5-l glass bottle.

The results in Table II were obtained using the recommended extraction procedure

TABLE I

THE CONCENTRATION OF URANIUM IN SEA WATER BY ISOTOPIC DILUTION–$AlPO_4$ CO-PRECIPITATION METHOD

Sample	*Uranium concentration (corrected for blank)*				*Mean value*	*Coefficient of variation*
'A'	3·33	3·33	3·34	3·34	$3{\cdot}3_4$ μg/l	0.17%
'B'	3·62	3·65			$3{\cdot}6_3$ μg/l	0.5%
Blank	0.07	0.09			0.08 μg	—
Calibration of tracer	2.87	2.87	2.87	2.89	2.87_4 μg/ml	0.4%

TABLE II

THE CONCENTRATION OF URANIUM IN SEA WATER BY ISOTOPIC DILUTION–8-HYDROXYQUINOLINE EXTRACTION METHOD

Sample	*Blank*	*Uranium concentration (corrected for blank)*			*Mean value*	*Coefficient of variation*
1. Weymouth Bay	0.0008 μg	3·30	3·32		$3{\cdot}3_1$ μg/l	0.28%
2. Bay of Biscay (4,210 m)	0.0025 μg	3·29	3·30	3·34	$3{\cdot}3_1$ μg/l	0.76%
3. Sample 16 (25°S., 145°W., 3,500 m)	0.0023 μg	2.99	2.99	3·01	$3{\cdot}0_0$ μg/l	0.47%
4. Sample 21 (43°50′S., 105°30′W.)	0.0019 μg	3·24	3·25	3·26	$3{\cdot}2_5$ μg/l	0.34%
5. Calibration of tracer	—	0.166	0.165	0.166	0.165_7 μg/g	0.38%

and an M.S.5 mass spectrometer. The Weymouth Bay coastal water quoted in Table II was a sample taken a year later than samples 'A' and 'B' in Table I, and was stored in a 45-l glass carboy. In view of the close agreement between the results for this sample and for sample A, even though quite different chemical separations were used, it seems probable that the small bottle containing sample B was contaminated. Samples 16 and 21 were kindly supplied by Dr. E. RONA, Oak Ridge Institute of Nuclear Studies. These results are given only as an illustration of the precision of the method, and are not included in the average value which is quoted later, for this refers only to English Channel and Bay of Biscay sea waters.

A discussion of the errors

The results are calculated from the equation

$$x = y \cdot \frac{R_{238} - T_{238}}{N_{238} - R_{238}} \cdot \frac{234\ N_{234} + 235 + 238\ N_{238}}{234\ T_{234} + 235 + 236\ T_{236} + 238\ T_{238}} \qquad (1)$$

where x is the mass of natural uranium to be measured, y is the mass of tracer added, and N, T and R refer to the isotope ratios (all with reference to the 235 isotope) for the normal, tracer and mixed element respectively. The same equation is used for the calibration of the tracer against the standard uranium solution, though x is then the known and y the unknown quantity. If it is assumed that the uranium in the standard solution and in the sea water has the same isotopic composition, the last factor in equation (1) is common to both the calibration and the determination and so cancels.

There are then three sources of error to be considered, (a) the determination of y the quantity of tracer, (b) contamination, and (c) random errors involved in the determination for sea water.

The error in the calibration of the tracer

This is made up as follows:

(1) Random error in the mass spectrometric calibration, standard error for the mean of 4 determinations equivalent to 0.19%. (2) Dilution errors, 2 standard flasks grade A limits —0.02% and 1 pipette, coefficient of variation —0.11%. (3) Mass of U_3O_8 in standard solution, coefficient of variation —0.07%. (4) Stoichiometry of U_3O_8.

The error in (4) is not easy to assess, but if it is assumed to be small[8], the overall coefficient of variation for the calibration is 0.24%.

Contamination from the reagents

A number of blank determinations using the oxine extraction were made in order to investigate the contamination. By changing the proportions of the reagents it was possible to show that most of the uranium blank came from the oxine itself, thus the blank correction for sample 1 in Table II refers to a smaller quantity of oxine than that used for samples 2, 3 and 4. Since the quantity of oxine which was used was kept constant in each series of measurements, there should be little variation in the blank correction, which was 0.0023 ± 0.0003 μg (mean of six measurements). The quantity of uranium which was measured in a determination was about 0.3 μg so that the blank correction represents about 0.8% of the amount measured, and the uncertainty in a single blank correction represents only 0.1%.

Random errors in a determination

Examination of equation (1) shows that any error in the measurement of the $^{238}U/^{235}U$ ratio for the mixture of sample and tracer will be magnified in the calculation of x, and that the magnification is a minimum for a value of $R_{238} \simeq \sqrt{N_{238}T_{238}}$. In this case, the optimum value for R is 2.8, whereas a ratio of about 1 was used in this work. The magnification factors for the ratios 2.8 and 1.0 are only 1.04 and 1.07 respectively, so that little precision is lost by using ratios of about unity, and the uncertainty in an amplifier range factor is then avoided.

The $^{238}U/^{235}U$ ratio for uranium in sea water was not determined, and the accepted value of 137.8 for natural uranium was assumed instead. It can be shown that an error of 1% in this assumed ratio will introduce one of only 0.015% into the measurement.

The coefficients of variation of the four results in Table II have a mean value of 0.46% and the mean coefficient of variation for a single determination, combined with a single blank measurement and including calibration errors is 0.52%. This value may be compared with a mean figure of 2.2% for the results reported by RONA, GILPATRICK AND JEFFREY[2].

THE FLUORIMETRIC METHOD

The very sensitive fluorimetric method for uranium has been used previously for the direct measurement of uranium in river waters[9]. However, this procedure could not be used for sea water without some modification for it involves the direct evaporation of the sample in a fluorimeter tray and the large residue from sea water (mainly sodium chloride) cannot be dissolved in the usual quantities of flux. A preliminary solvent extraction of the uranium into chloroform as its oxine complex was again used and ^{237}U tracer was employed to measure the chemical yield.

Experimental method

The solvent extraction of the uranium was carried out in a similar way as in the isotopic dilution method. The following differences should be noted, however. 100 ml of the sample was taken and mixed with about 0.1 ml of a ^{237}U tracer solution (containing ~0.1 μC). The preparation of ^{237}U has already been described[5]. The solution was *boiled* and then left overnight to allow the ^{237}U to exchange with the natural uranium. The chloroform extracts were collected together and made up to 10 ml in a standard flask. 2 ml of this solution was transferred to a cylindrical polythene container ('Polytainer') placed in a well type crystal in a γ-counter, and at least 10,000 counts were recorded for this and for a standard solution. The chemical yield was measured in this way. The fluorimetric estimation was carried out as follows:

Place three clean fluorimeter dishes in position on a hot peripheral heating block[9] and add a total of 2 ml of the chloroform extract to each, adding 0.5 ml at a time, and allowing the chloroform to evaporate completely between the additions. Add 0.25 ml of a solution of magnesium carbonate in glacial acetic acid (1 mg/ml magnesium) adding the liquid slowly to prevent the dissolving 8-hydroxyquinoline from creeping up the sides of the platinum dish. Then add 0.5 ml of a solution of uranium containing 0.1 μg/ml, as an internal standard, to one dish only. Continue heating, and when all the dishes are dry, gently flame off the organic matter and bring each dish momentarily to a red heat. Add 0.5 g of a mixed sodium carbonate–fluoride flux to each dish and place in position on a platinum gauze over a gas burner. Fuse at the lowest possible temperature, and keep molten for about five minutes, swirling the melt occasionally. Allow the dishes to cool slowly, and when they are quite cold, measure the fluorescence in a fluorimeter. Re-fuse briefly, allow to cool, and check that the maximum degree of fluorescence has been reached. Calculate the uranium content of the sample by the standard method[9].

Results

Six sea water samples, collected from various depths in the Bay of Biscay, were analysed by the fluorimetric method, and the results are given in Table III.

Earlier experience with the fluorimetric method showed that it was desirable to measure the chemical yield with a radioactive tracer, for the results which were obtained without the addition of tracer were significantly lower than those values obtained by other methods. When the chemical yields were measured with the ^{237}U tracer it became clear that it was essential to use such a tracer, for chemical yields as low as 74% were recorded. Unless a tracer is used it must be assumed that the results may be systematically too low.

A DISCUSSION OF THE RESULTS OBTAINED BY THE DIFFERENT METHODS

The results of the analyses of a number of sea waters by the isotopic dilution (I.D.), pulse polarographic (P.P.) and fluorimetric methods (F) are summarised in Table III. It can be seen that there is no difference within the limits of experimental error between the results obtained for English Channel (coastal) and Bay of Biscay (deep sea) samples. Similarly, if there is any variation of the uranium concentration with depth, it is so small as to be less than the experimental errors in both the polarographic and fluorimetric methods, and only accurate analyses made by the isotopic dilution

TABLE III

A COMPARISON OF THE RESULTS OF ANALYSES OF SEA WATER BY THREE METHODS

Origin of sample	*Method of analysis*		
	Isotopic dilution, μg/l uranium	*Pulse polarography, μg/l uranium*	*Fluorimetry with tracer, μg/l uranium*
1. Bay of Biscay, stored in polythene			
1. 7 metre depth	—	$3{\cdot}5 \pm 0.2$	$3{\cdot}5 \pm 0.3$
2. 570 metre depth	—	$3{\cdot}5 \pm 0.2$	$3{\cdot}0 \pm 0.8$
3. 975 metre depth	—	$3{\cdot}6 \pm 0.2$	$3{\cdot}2 \pm 0.3$
4. 1990 metre depth	—	$3{\cdot}2 \pm 0.2$	$3{\cdot}1 \pm 0.3$
5. 2815 metre depth	—	$3{\cdot}3 \pm 0.2$	$3{\cdot}4 \pm 0.2$
6. 4210 metre depth	$3{\cdot}3_1 \pm 0.06$	$3{\cdot}4 \pm 0.2$	$3{\cdot}3 \pm 0.4$
		Mean = $3{\cdot}4_1 \pm 0.17$[a]	Mean = $3{\cdot}2_5 \pm 0.23$[a]
2. Weymouth Bay			
1. Stored in polythene	$3{\cdot}3_4 \pm 0.04$	—	—
2. Stored in glass	$3{\cdot}6_3 \pm 0.06$[b]	—	—
3. Stored in glass	$3{\cdot}3_1 \pm 0.04$	—	—
4. Stored in glass	—	$3{\cdot}3_7 \pm 0.08$	—

[a] Estimated from the actual spread of the results.

[b] Assumed to be a contaminated sample.

method are likely to detect any variation. The errors which are quoted are 3 times the estimated standard error of the mean value.

The results for Bay of Biscay waters by the three different methods are $3.3_1 \pm 0.06$ (I.D. — 3 analyses), $3.4_1 \pm 0.1_7$ (P.P. — 9 analyses, see Ref.[5]) and $3.2_5 \pm 0.2_3$ (F — 6 analyses). Assigning equal weight to each of these values gives a mean value of 3.32 µg of uranium per l. In a similar way an average value of 3.3_4 µg/l is obtained for the Weymouth Bay water, and on assuming no significant difference between the waters from the two sampling points, an overall average of $3.3_3 \pm 0.08$ µg/l is found. This value is in good agreement with that of 3.3_9 µg/l (3.31 µg/kg) found by RONA, GILPATRICK AND JEFFREY[2] for waters from the North Atlantic and the Gulf of Mexico.

A COMPARISON OF THE METHODS OF ANALYSIS

The three methods may be compared on the basis of the precision and accuracy of each, the man hours and the time taken to achieve such accuracy and the cost of the equipment. It is first necessary to distinguish between the *time* taken for an analysis and the man hours (or effort) involved. The time for an analysis may be taken as the time interval between the receipt of a sample and the reporting of the result. The effort, however, is not proportional to the time because in all three methods it is necessary to allow the same time (1 day) for isotopic equilibrium to be established. Because of this, the disparity in the time taken by the various analytical methods is much less than the disparity in the man hours involved.

The three methods, as they have been described in this and in an earlier paper[5], have been taken as the basis for the comparisons and the results are given in Tables IV and V. Table IV shows an analysis of the way in which the time and effort is distributed amongst the various operations, whilst Table V gives a comparison of the methods. No attempt has been made to take account of the numerous variations which

TABLE IV

THE TIME AND EFFORT REQUIRED FOR VARIOUS OPERATIONS

Operation	*Pulse polarographic method*	*Isotopic dilution method*	*Fluorimetric method*
1. Addition of tracer and isotopic exchange			
Time	1 day	1 day	1 day
2. Extraction of Uranium	2 extractions, 1 back extraction, and 2 evaporations (usually 6 samples simultaneously)	1 extraction and 2 evaporations (5 samples simultaneously)	1 extraction and 1 evaporation (1 sample at a time)
Effort	8 man hours per sample	2½ man hours per sample	2 man hours per sample
3. Measurement of radiochemical yield	100,000 counts on standard and unknown at 2000 c.p.m.	—	10,000 counts on standard and unknown at 200 c.p.m.
Effort	2 man hours per sample	nil	2 man hours per sample
4. Measurement of total uranium			
Effort	5 man hours per sample	1½ to 2 man hours per sample	1½ man hours per sample

Note: blank determinations count as one actual analysis.

are possible — for example, variations in the number of samples extracted simultaneously, or in the division of time between extraction and measuring processes.

In interpreting the data given in Tables IV and V, the following points should be borne in mind:

1. In all the methods the measurements were repeated as often as possible in order to obtain a high precision. With the mass spectrometer, for example, about 15 complete scans were recorded for any one sample to give about 30 estimates of the ^{238}U/^{235}U ratio. Clearly the precision could be improved by recording more ratios, but to achieve a significant improvement would require a substantial increase in the time needed both for recording and for measuring ratios. The precision of the fluorimetric method is not improved by making more measurements on each tray, but only by making measurements on a greater number of melts since the irreproducibility of the fusion is the limiting factor. The number of melts which can be made is limited by the amount of uranium extracted. In the polarographic method the number of measurements on each sample is limited by deterioration of the final solution when left in the cell overnight.

TABLE V

A COMPARISON OF THE THREE METHODS OF ANALYSIS

	Pulse polarographic method	*Isotopic dilution method*	*Fluorimetric method*
1. Precision of method:			
For radiochemical yield	1.1%	—	1.3%
For uranium estimation	0.7%	0.52%	3%
Overall Coefficient of Variation	1.4% (estimated)	0.52% (measured)	5% (measured)
2. Minimum *time* for analysis	3 days	2 days	1.5 days
3. Effort per sample	15 man hours	$\sim$5 man hours	$\sim$6 man hours
4. Size of sample required	4 l	100 ml	100 ml

2. No account has been taken of the time needed for the calibration of the ^{235}U tracer in the isotopic dilution method, or of the time required to prepare ^{237}U for the other methods. The calibration need be done only infrequently, and the preparation of enough ^{237}U for 2 weeks work takes about 1 day, once the ion-exchange column containing ^{241}Pu has been set up. Whilst both the tracer calibration and ^{237}U separations would add considerably to the time taken for a single analysis, they form only an insignificant part of the time involved in a large number of analyses.

3. The time taken in measuring the background count rate has not been included in the time spent in counting the ^{237}U, since it is usual to record the background count rate over a long period of time whilst other work is being done.

These tables show that the isotopic dilution method is to be preferred, but this involves expensive equipment. The cost of equipment for this method may be reduced by using a smaller and less sensitive mass spectrometer (not available commercially), but this would involve using larger sea water samples (1–2 l) and consequently a relatively cumbersome and time-consuming chemical procedure.

Although the costs for equipment in the other two methods are lower, these methods could only be considered as replacements fort he isotopic dilution method if the precision of the results could be improved. The higher overall coefficient of variation for the results by polarography arises mainly from errors in counting the ^{237}U. The observed coefficient of variation for a single count is 0.8%. As the coefficient of variation calculated for 100,000 counts is only 0.3%, the greater part of the counting error must arise from errors in transferring the sample solution to a polythene container and from irreproducibility in positioning the container in the well of the NaI crystal of the γ-counter. By exercising greater precautions it may be possible to improve the precision in this part of the determination. The coefficient of variation of 0.7% for recording and measuring the polarographic peaks is based on a measured coefficient of variation of 1% for a single measurement of peak height. It might be possible to improve on this by paying more attention to the reproducibility of the conditions within the polarographic cell, since the instrument is more reproducible than this.

In the fluorimetric method, the value of the coefficient of variation of the counting operation could be reduced to about 0.8% by taking greater precautions, but the precision of the fluorimetric measurement could only be improved by analysing each sample many times. It would be necessary to make at least 100 determinations to approach the precision of the isotopic dilution method.

CONCLUSIONS

It has been shown that there are at least three methods which can be used to obtain accurate values for the uranium content of sea water samples. If the cost is of no consequence, the isotopic dilution method is the best of the methods examined in this work.

The analyses which have been made for sea water samples from Weymouth Bay and from the Bay of Biscay show little difference in the uranium concentration and give a mean value of $3.3_3 \pm 0.08$ μg per l.

ACKNOWLEDGEMENTS

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SUMMARY

A stable isotopic dilution method and a fluorimetric method for the measurement of the concentration of uranium in sea water are described. In both methods the uranium is extracted from the sea water into chloroform using 8-hydroxyquinoline. ^{237}U is used as a tracer in the fluorimetric method. The results obtained by these two methods and by a pulse polarographic method are compared, and give a mean value of $3.3_3 \pm 0.08$ μg per l for the uranium content of samples of English Channel and Bay of Biscay water. The precision of the methods improves in the order fluorimetry, pulse polarography, isotopic dilution.

RÉSUMÉ

Les auteurs ont effectué une étude de comparaison entre la méthode par dilution isotopique et la méthode fluorimétrique pour le dosage de l'uranium dans l'eau de mer. Dans les deux cas, on procède à l'extraction du complexe uranium-hydroxy-8-quinoléine dans le chloroforme. Les résultats ont été comparés avec ceux obtenus par une méthode polarographique.

ZUSAMMENFASSUNG

Beschreibung einer Isotopen-Verdünnungsmethode und einer fluorimetrischen Methode zur Bestimmung von Uran in Meerwasser. Die Abtrennung aus dem Meerwasser erfolgt durch Extraktion des Uran-8-Oxychinolin Komplexes mit Chloroform. Die erhaltenen Werte werden mit den Ergebnissen einer polarographischen Methode verglichen.

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DECOMPOSITION OF FERROCYANIDE IN ANALYSIS

IV. NEW SPOT TEST FOR GOLD*

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Under ultraviolet light[1] and in the presence of certain cations (Hg[2–5], Au[6,7], Pt[6], Ag[4,5], Pd[8]) ferrocyanide(II) and nitrosobenzene react to yield the violet pentacyanide complex[3,9]:

$$[Fe\,(CN)_6]^{-4} + NO\cdot C_6H_5 \xrightarrow[Au,\ Hg]{} [Fe\,(CN)_5\cdot NO\cdot C_6H_5]^{-3} + CN^-$$

Since this complex is intensely coloured, methods based on this reaction are very sensitive. For example, the method for spectrophotometric determination of mercury[3] can be applied to concentrations as small as 10^{-7} moles of mercury/l, while methods for the photometric determination of gold[7] (0.2–13 p.p.m.) and palladium[8] ($5\cdot 10^{-6}$–$8\cdot 10^{-4}$ moles/l) are only slightly less sensitive.

Spot tests based on the same principle have the following sensitivities:

Hg[5]: 0.002 μg/drop; Ag[10]: 0.004 μg/drop;

Pd[8]: 0.02 μg/drop; some aromatic nitrosocompounds[11]: 0.02–1 μg/drop.

The spot test described in the present paper has the sensitivity of 0.05 μg/drop and it is suitable for the detection of gold in solutions containing foreign cations.

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* Part III in *Mikrochim. Acta*, (1960) 586.

EXPERIMENTAL

Reagents

$HAuCl_4$: A 0.005-*M* solution was used as stock solution. Diluted solutions were prepared fresh every day by dilution with distilled or redistilled water in Pyrex or Jena glassware.

$K_4[Fe(CN)_6]\cdot 3H_2O$: A 0.5% solution was used. For the detection of gold at concentrations near the limit of sensitivity, the solution must be prepared fresh daily and kept away from direct sunlight.

$C_6H_5\cdot NO$: A saturated aqueous solution was obtained by dissolving an excess of the substance in distilled water at 70° (on a water bath). The solution must be prepared fresh every 8 to 10 days. The nitrosobenzene was prepared by oxidation of aniline with Caro's acid[12].

Acetate buffer: 1-*M* solution, pH 5.0.

Solution "A": A 4 to 1 mixture of nitrosobenzene and acetate buffer solutions.

TABLE I

INTERFERENCE OF CATIONS

Concentration of Au: 0.5 μg/drop ($5\cdot 10^{-5}$ moles/l)

Cation	*Conc. of cation in moles/l or Au : Me (by weight)*	*Effect on sensitivity*
K	0.10	None
Na	0.10	None
Mg	0.03	None
Ca	0.10	None
Sr	0.10	None
Ba	0.10	None
Zn	1 : 80	Strong decrease[a]
Mn	1 : 80	Strong decrease[a]
Co	1 : 20	Considerable decrease[a]
Ni	1 : 20	Considerable decrease[b]
Cr^{+3}	1 : 20	Considerable decrease
Al	1 : 80	Strong decrease
	1 : 20	Considerable decrease
Fe^{+3}	1 : 20	Strong decrease[a]
	1 : 10	Considerable decrease[a]
As(AsO_2^-)	1 : 20	Considerable decrease
Cd	1 : 80	Slight[a]
Cu^{+2}	1 : 20	Slight. After warming it is necessary to add NaOH.
Bi	1 : 20	Strong decrease
	1 : 10	Considerable decrease
Pb	1 : 80	Considerable decrease
U(UO_2^{+2})	1 : 40	Considerable decrease
	1 : 20	Slight
Pt($PtCl_6^{-2}$)	$5\cdot 10^{-3}$	Slight. No effect on decomposition!
Hg	0.01	Hg gives the same effect but can be
	$4\cdot 10^{-5}$	masked by KI. KI must be added.
Ag	0.01	The effect is almost completely prevented. Slight influence if KI added.
	$1\cdot 10^{-4}$	No effect in presence of KI.

[a] 3 drops of $K_4[Fe(CN)_6]$.

[b] 2 drops of $K_4[Fe(CN)_6]$.

PROCEDURE

A drop of $K_4[Fe(CN)_6]$ solution was placed in the depression of a porcelain spot plate followed by a drop of solution "A", and then a drop of the test solution. A parallel blank test was run with a drop of distilled water. After a short period, or on heating to about 30 to 40°, a pink or violet colour appeared, while the blank remained colourless or faintly yellow. The colour appeared very quickly on heating, but its intensity was not increased by further heating. Sunlight has an effect similar to that of the gold ion, hence the experiments must be conducted in the shade or in the light of an incandescent lamp.

Sensitivity

The action of gold on ferrocyanide is strongly affected by the acidity of the solution; for optimum sensitivity the pH must be correct. An acetate buffer maintaining a pH of 5.0 has proved best, pH 4.1 and 6.2 giving significantly lower sensitivities. It has been also ascertained that optimum sensitivity is obtained with a 0.5% solution of potassium ferrocyanide and a saturated solution of nitrosobenzene.

The sensitivity of this spot test for the pure system was investigated with the following results:

Limit of identification 0.05 μg/drop (0.05 ml) and
Concentration limit 1 : 1,000,000.

Interference of cations

Of the cations investigated (Table I) only mercury and silver react analogously; mercury in low concentrations does not react immediately at room temperature, and silver does not react even after protracted waiting, hence gold can be detected in the presence of those cations. On heating, both metals give stronger colorations, which make the detection of gold unreliable. Previous investigations[5,10] have shown that iodides in high concentrations completely inhibit the reactions of mercury and silver; further tests showed the mercury and silver interferences with the reaction for gold can be eliminated by the addition of iodides. Moreover, this addition accelerates the reaction with gold, so that no heating is necessary.

Heavy metals that yield coloured precipitates with ferrocyanide (Fe^{+3}, Cu^{+2}, UO_2^{+2}) also interfere with the detection of gold, but this interference can be readily eliminated by warming during the test, and then destroying the precipitate by making the solution alkaline (see Table I). Unfortunately, this expedient breaks down when the concentration of the interfering ion is too high.

Large amounts of certain cations, although they do not give intensely coloured precipitates, considerably lower the sensitivity of the test; others have no effect even at very high concentrations (see Table I).

Interference of anions

The effect of some anions on the activity of gold has also been studied. Most anions do not interfere even at high concentrations. Thiosulphate, sulphite and cyanide at high concentrations considerably lower the sensitivity, and may even inhibit the action of the gold ion. Iodides accelerate the reaction significantly, presumably by reducing Au^{+3} to Au^{+}. The results of these experiments are summarized in Table II.

TABLE II

INTERFERENCE OF ANIONS

Concentration of Au: 0.5 μg/drop ($5 \cdot 10^{-5}$ moles/l)

Anion	*Conc. of anion in moles/l*	*Effect on sensitivity*
NO_3^-	0.10	None
SO_4^{-2}	0.01	None
CH_3COO^-	0.10	None
Cl^-	0.10	Slight
	0.01	None
Br^-	0.10	Slight
	0.01	None
I^-	0.10	The reaction is faster and more sensitive
CNS^-	0.10	Slight
CN^-	0.01	Strong decrease
$B_4O_7^{-2}$	0.01	None
$C_2O_4^{-2}$	0.10	Slight
SO_3^{-2}	0.10	The reaction is completely inhibited
	$2 \cdot 10^{-4}$	Considerable decrease
HPO_4^{-2}	0.10	Slight
$S_2O_3^{-2}$	0.01	The reaction is completely inhibited
	$1 \cdot 10^{-3}$	The reaction is completely inhibited
	$1 \cdot 10^{-4}$	Strong decrease

SUMMARY

A very selective spot test for gold has been developed based on the effect of gold(III) on the decomposition of ferrocyanide in the presence of nitrosobenzene. The sensitivity is 0.05 μg/drop and the concentration limit 1 : 1,000,000. Mercury and silver react analogously, but can be masked with iodide, which also improves the sensitivity. Interferences of iron(III), copper(II) and uranyl ion can be avoided.

RÉSUMÉ

Les auteurs ont mis au point une nouvelle réaction à la touche, sensible et sélective, pour l'identification de l'or. Elle est basée sur l'influence de Au^{+3} sur la décomposition des ferrocyanures, en présence de nitrosobenzène.

ZUSAMMENFASSUNG

Es wird eine neue Tüpfelprobe für Gold beschrieben. Die empfindliche und selektive Reaktion beruht auf dem Einfluss von Au^{+3} auf die Zersetzung von Ferrocyanid in Gegenwart von Nitrosobenzol.

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THE INFLUENCE OF ACIDS AND SALTS ON THE USE OF CHROMOUS CHLORIDE AS A REDUCING TITRANT

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The importance of chromous chloride as a reducing titrant for the determination of metal ions is well known. The early work of ZINTL *et al.*[1] consisted mainly of determining the optimum conditions whereby chromous solutions could be successfully used for the determination of mercury(II), iron(III), silver(I) and gold(III). In recent years, MURAKI[2] and LINGANE AND NIEDRACH[3] have carried out studies on similar lines. LINGANE AND NIEDRACH used a platinum indicator electrode to study the reduction of quadri- and hexavalent selenium and tellurium with chromous ions, and attempted to find conditions of acidity under which accurate results could be obtained.

Although many workers have employed the chromous–chromic system in potentiometric work, very little has been done to investigate systematically the factors influencing such titrations. This communication deals with our investigations on potentiometric titration of copper sulphate with chromous chloride solution in presence of various acids and their salts. The probable role of hydrogen and chloride ions is also discussed.

EXPERIMENTAL

Chromous chloride solution

The behaviour and stability of chromous solutions are likely to vary from sample to sample depending on the mode of preparation, the presence of foreign ions and the method of storage; a special method was therefore used for the preparation of the solution free from foreign ions, and for its storage. The method recommended by BALTHIS AND BAILAR[4] with a slight modification was followed. Chromic chloride was reduced with zinc and hydrochloric acid and the chromous chloride thus obtained was converted to chromous acetate by adding sodium acetate, an inert atmosphere being maintained. The acetate was then washed free of zinc salt (by suction device under CO_2 atmosphere) and dissolved in air-free, ice-cold 1.0 N hydrochloric acid. The solution so obtained contained an equivalent amount of acetic acid as a product of the reaction. To obtain a completely 'neutral' solution twice the volume of freshly distilled ice-cold alcohol was added when a copious precipitate of chromous chloride separated. It was filtered by suction and repeatedly washed with ice-cold 90% alcohol. The precipitate was then dissolved in the required amount of ice-cold water to give the deep blue chromous chloride solution free from any foreign ion. This method gave the purest aqueous solution, which was stored in a STONE[5] type bottle and remained stable for months.

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Strength of chromous chloride solution

The chromous chloride solution must be standardized regularly; a quick and accurate method was evolved. 5.0 ml of 0.1 *N* potassium permanganate acidified with 15.0 ml of 2 *N* sulphuric acid was transferred to a 100-ml beaker and covered with a layer (about 0.5 cm thick) of kerosene. 2.0 ml of chromous chloride solution was then transferred to the permanganate keeping the tip of the burette under the layer of kerosene. The mixture was stirred and set aside for 5 min to ensure complete oxidation of chromium(II), and the excess of permanganate was titrated potentiometrically with 0.05 *N* ferrous sulphate (Fig. 1). For estimating total chromium the method adopted by FORBES AND RICHTER[6] was employed.

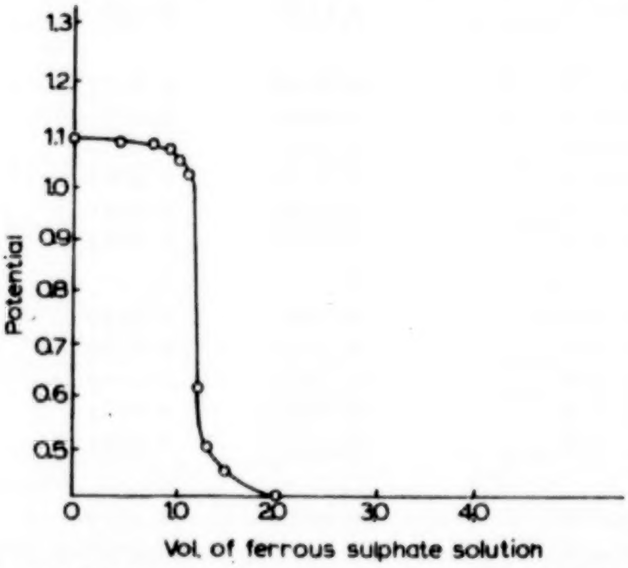

Fig. 1. Standardisation of chromous chloride solution.

PROCEDURE

A Tinsley Potentiometer type 3387B with lamp-scale, galvanometer arrangement was used for potential measurements. The electrodes used were a smooth platinum wire and Beckman Fibre type calomel electrode. 5.0 ml of 0.1 *N* copper sulphate solution was placed in an air-tight cell. Varying amounts of the reagents were added and the total volume was made up to 30.0 ml with the requisite amount of air-free water. The air in the cell was then completely displaced by passing a rapid current of nitrogen for about 15 min. The contents in the cell were then titrated with chromous chloride using the micro-burette attachment. Some typical titration curves are given in Fig. 2 and the observations are summarised in Table I.

DISCUSSION

The second break of the titration curves was usually pronounced, but sharp breaks in the first stage were only obtained in presence of hydrochloric acid and potassium chloride separately or together. At high concentrations of this acid and salt the white precipitate of cuprous chloride did not appear and sharp breaks were obtained in the first stage of reduction. With sulphuric acid, the second break was fairly sharp, but with the sodium salt or a mixture of the acid and the salt, typical titration curves were not obtained. In a large number of experiments it was found that although the chloride ions (also from potassium or ammonium chloride) gave typical titration

TABLE I

Strength of $CrCl_2$ solution = 0.2739 *M* (permanganate method); Cr^{+3}/Cr^{+2} = 0.1508; temp. = 25 ± 0.1°

Reagent	Conc. of the reagent	Strength of $CrCl_2$ from		Nature of curve[a]	
		1st break	2nd break	1st break	2nd break
temp. = 25 ± 0.1°					
1. ('Neutral' solution)		0.2858	0.2739	F.S.	S.
2. HCl	0.1 *N*	0.2809	0.2739	S.F.	S.
HCl	0.2 *N*	0.2777	0.2688	F.S.	S.
HCl	0.5 *N*	0.2739	0.2667	S.	S.
HCl	1.0 *N*	0.2739	0.2667	S.	S.
HCl	2.0 *N*	0.2748	0.2631	S.	S.F.
3. KCl	0.1 *N*	0.2809	0.2777	F.	S.
KCl	0.2 *N*	0.2809	0.2739	F.S.	S.
KCl	0.5 *N*	0.2777	0.2681	S.	S.
KCl	1.0 *N*	0.2777	0.2667	S.	S.
KCl	1.5 *N*	0.2732	0.2631	S.	S.
KCl	2.0 *N*	0.2777	0.2613	S.	S.
4. H_2SO_4	0.1 *N*	0.2703	0.2739	Q.F.	F.S.
H_2SO_4	0.2 *N*	0.2732	0.2739	Q.F.	S.
H_2SO_4	0.5 *N*	(0.2703)	0.2703	Q.F.	S.
H_2SO_4	1.0 *N*	(0.2631)	0.2683	Q.F.	S.
H_2SO_4	2.0 *N*	(0.2631)	0.2681	Q.F.	S.
5. Na_2SO_4	0.1 *N*	(0.2631)	0.2717	F.	S.
Na_2SO_4	0.5 *N*	—	0.2703	Q.F.	S.
Na_2SO_4	1.0 *N*	—	0.2717	Q.F.	S.
Na_2SO_4	1.5 *N*	—	0.2703	Q.F.	S.
6. HAc	0.1 *N*	(0.2631)	0.2703	F.S.	S.
HAc	0.5 *N*	(0.2564)	0.2717	F.	S.
HAc	1.0 *N*	—	0.2703	Q.F.	S.
HAc	2.0 *N*	—	0.2718	Q.F.	F.S.
7. NaAc	0.1 *N*	—	(0.2597)	Q.F.	F.
NaAc	0.2 *N*	—	—	Q.F.	Q.F.
8. KCl + HCl	0.1 *N*, 0.1 *N*	0.2758	0.2739	F.S.	S.
KCl + HCl	1.0 *N*, 0.1 *N*	0.2748	0.2667	S.	S.
KCl + HCl	0.1 *N*, 1.0 *N*	0.2732	0.2667	Q.F.	S.
KCl + HCl	1.0 *N*, 1.0 *N*	0.2748	0.2631	Q.S.	S.
9. H_2SO_4 + Na_2SO_4	0.1 *N*, 0.1 *N*	0.2631	0.2703	F.	S.
H_2SO_4 + Na_2SO_4	0.1 *N*, 1.0 *N*	0.2564	0.2739	Q.F.	S.
H_2SO_4 + Na_2SO_4	1.0 *N*, 0.1 *N*	(0.2564)	0.2739	Q.F.	S.
H_2SO_4 + Na_2SO_4	1.0 *N*, 0.7 *N*	—	—	Q.F.	S.
10. HAc + NaAc	0.1 *N*, 0.1 *N*	0.2564	0.2703	Q.F.	S.
HAc + NaAc	1.0 *N*, 0.1 *N*	—	(0.2667)	Q.F.	F.
11. KCl + HAc	0.1 *N*, 0.1 *N*	0.2631	0.2703	S.	S.
KCl + HAc	1.5 *N*, 0.5 *N*	0.2739	0.2631	S.	S.
KCl + HAc	0.5 *N*, 1.5 *N*	0.2703	0.2667	S.	S.
KCl + HAc	1.0 *N*, 1.0 *N*	0.2703	0.2564	S.	S.

TABLE I (continued)

Reagent	Conc. of the reagent	Strength of $CrCl_2$ from		Nature of curve[a]	
		1st break	2nd break	1st break	2nd break
temp. = *55 ± 0.1°*					
1. ('Neutral' solution)		0.2703	0.2703	F.	S.
2. HCl	0.5 *N*	0.2703	0.2667	S.	S.
HCl	1.0 *N*	0.2703	0.2667	S.	S.
HCl	2.0 *N*	0.2667	0.2603	S.	S.
3. KCl	0.5 *N*	0.2777	0.2703	F.	S..
KCl	1.0 *N*	0.2703	0.2703	F.S.	S.
KCl	2.0 *N*	0.2703	0.2597	F.S.	F.S.
4. KCl + HCl	1.0 *N*, 1.0 *N*	0.2703	0.2564	Q.S.	F.S.
5. H_2SO_4	0.5 *N*	(0.2564)	0.2631	Q.F.	S.
H_2SO_4	1.5 *N*	—	0.2667	Q.F.	S.
6. HAc	1.5 *N*	(0.2703)	0.2667	F.	F.
7. H_2SO_4 + Na_2SO_4	1.0 *N*, 1.0 *N*	(0.2500)	0.2703	F.	F.
8. KCl + HAc	0.5 *N*, 1.0 *N*	0.2732	0.2703	S.	S.
KCl + HAc	1.0 *N*, 1.0 *N*	0.2732	0.2739	Q.S.	S.
9. NH_4Cl	0.5 *N*	0.2703	0.2667	S.	S.
NH_4Cl	1.5 *N*	0.2732	0.2631	S.	F.
10. NH_4Cl + HAc	0.5 *N*, 1.0 *N*	0.2703	0.2667	F.	S.
NH_4Cl + HAc	1.0 *N*, 1.0 *N*	0.2732	0.2631	F.	S.

[a] F = flat; S = sharp; Q.F. = quite flat; Q.S. = quite sharp; S.F. = slightly flat; F.S. = fairly sharp.

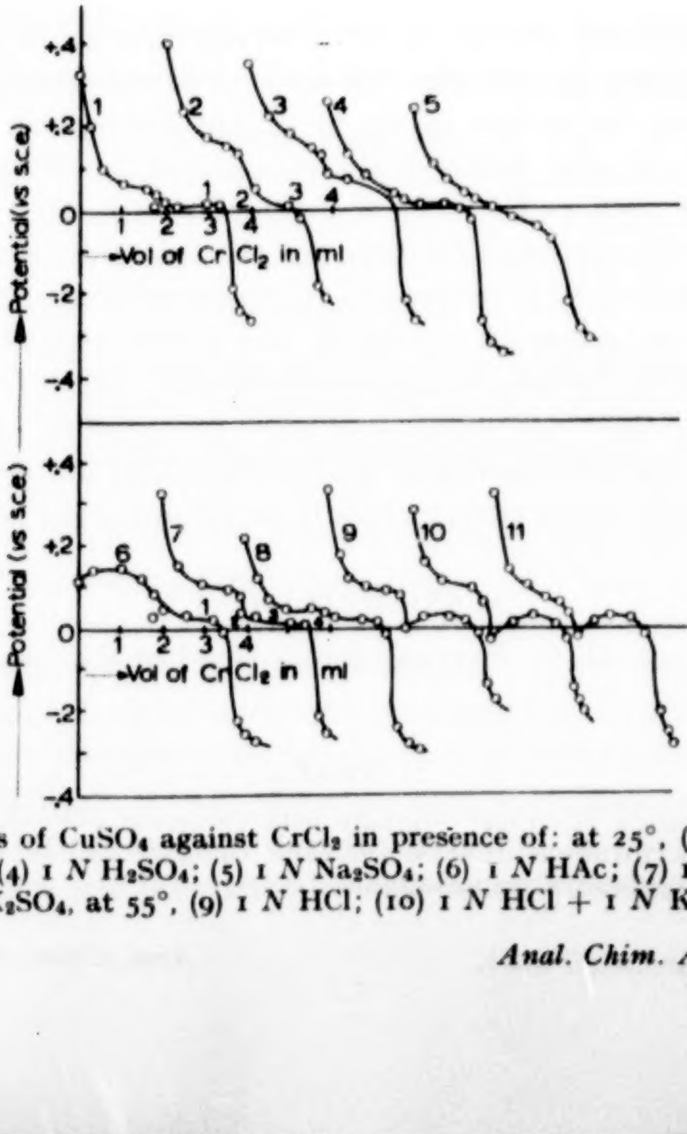

Fig. 2. Titration curves of $CuSO_4$ against $CrCl_2$ in presence of: at 25°, (1) neutral medium; (2) 1 *N* HCl; (3) 1 *N* KCl; (4) 1 *N* H_2SO_4; (5) 1 *N* Na_2SO_4; (6) 1 *N* HAc; (7) 1 *N* KCl + 1 *N* HCl; (8) 1 *N* H_2SO_4 + 1 *N* K_2SO_4, at 55°, (9) 1 *N* HCl; (10) 1 *N* HCl + 1 *N* KCl; (11) 1 *N* NH_4Cl.

curves with two breaks, the presence of acids was highly desirable since this helped in the rapid attainment of a steady electrode potential.

The potentials of the various systems involved are:

1. $Cu^{+2} + e \rightleftharpoons Cu^{+}$ $E = 0.153$ V
2. $Cu^{+} + e \rightleftharpoons Cu$ $E = 0.521$ V
3. $Cr^{+3} + e \rightleftharpoons Cr^{+2}$ $E = +0.411$ V

The equivalence potential for system (*a*), first break $= (-0.153 + 0.140)/2 = 0.1285$V and for system (*b*), second break $= (-0.521 + 0.410)/2 = -0.055$ V. Although the theoretical values of the equivalence potentials at the two stages of the reaction were not strictly realised, the deviations did not affect the determination of the strength of the solution. Results coinciding with the actual value (0.2739 *M* as determined by the permanganate method) were achieved by considering the second stage for lower concentrations of HCl or KCl or both, while higher concentrations of these electrolytes gave concordant values even at the first stage of reduction. With the other electrolytes, only in a few scattered cases (low concentrations of H_2SO_4 and Na_2SO_4 and KCl at the first stage, KCl and at 58°, and NH_4Cl and HAc) were the values obtained approximately the same as the actual concentration of chromous chloride solution. Titrations at high temperatures (as recommended by other workers) did not appear to be preferable; at high temperatures the values obtained were lower than the actual values even though the high temperature helped in the rapid attainment of equilibrium.

Since the reaction $Cr^{+2} + Cu^{+2} \rightleftharpoons Cu^{+} + Cr^{+3}$ involves two unstable ions, the necessary condition for carrying out the titration appears to be to stabilise both of them. This is possible with complexing agents[6,7] such as KCl, HCl, NH_4Cl etc.; better results can, however, be achieved when sufficient hydrogen ions are also added to prevent hydrolysis.

In determining conditions for the use of chromous chloride in oxidation–reduction titrations, it is necessary to consider not only factors influencing the stability of chromous ions but also the nature of the metal ion undergoing reduction. Addition of HCl or KCl would not only influence the stability of the chromous ions but would also form complexes[8] such as K_2CuCl_3, K_3CuCl_4, H_2CuCl_3, etc. with copper(I). It is highly probable that favourable conditions for the appearance of the first break are achieved by the formation of these complexes. An interesting and new aspect in these titrations is the role of ammonium chloride, which was found to be quite useful in the titrations. Results on the behaviour of chromium(II) and (III) at the dropping mercury electrode confirm this[9]; the anodic half wave potential for chromium(II) in ammonium chloride was higher than that in hydrochloric acid so that ammonium ions exerted a greater influence than hydrogen ions in determining the nature of the reaction.

ACKNOWLEDGEMENT

Thanks are due to Prof. M. O. FAROOQ, lately Head of the Chemistry Department, for providing facilities.

SUMMARY

The potentiometric titration of copper sulphate with chromous chloride solution is studied in presence of varying concentrations of acids and salts. Chloride ions are essential and hydrogen ions desirable. High temperatures are unsuitable.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'influence d'acides et de divers sels sur le comportement du sulfate de cuivre, lors de titrages potentiométriques au moyen de chlorure de chrome(II).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss von Säuren und verschiedener Salze bei der potentiometrischen Titration von Kupfersulfat mit Chrom-(II)-chlorid.

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DOSAGE DIRECT DE CALCIUM ET DE MAGNÉSIUM EN PRÉSENCE DE FER, ALUMINIUM ET TITANE PAR LE SEL DISODIQUE DE L'ACIDE ÉTHYLÈNEDIAMINETÉTRACÉTIQUE (EDTA)

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INTRODUCTION

Les dosages du calcium et du magnésium à l'aide de réactifs modernes, en passe de devenir ,,classiques'', tels que le complexon III ont fait l'objet de très nombreuses publications examinées notamment dans les ouvrages de base de PRIBIL, SCHWARZENBACH ET FLASCHKA[1-3].

Parmi les avantages de cette méthode il faut citer: une certaine spécificité, une grande rapidité, une bonne sensibilité et précision.

Toutefois, dans le cadre des analyses de ces deux éléments, dans les produits tels que les silicates naturels (argiles, kaolins, feldspath, etc. . .) ou complexes (émaux, frittes, etc. . .), ce dosage devient nettement plus long car il nécessite: d'une part la séparation préalable de l'aluminium, du fer, du titane et éventuellement du manganèse et du chrome, qui, comme on le sait, gênent ce dosage et, d'autre part, l'élimination des sels ammoniacaux formés au cours de cette opération. La précipitation des hydroxydes des éléments cités par les méthodes classiques à l'ammoniaque[4,5], peut entraîner une certaine absorption du calcium sur le précipité formé et apporter dans le cas de l'analyse de faibles teneurs de calcium, un élément d'erreur. La séparation plus sélective des hydroxydes par l'ammoniaque -urée, préconisée par le C.O.B.E.A.[6], n'entraîne pratiquement pas le calcium comme nous avons pu le constater sur des solutions synthétiques[7]. Cependant, même dans ce cas, les fortes quantités d'urée et d'ammoniaque introduites dans le milieu, obligent l'analyste à procéder à leur élimination toujours longue et fastidieuse.

Cet état de choses nous a incités à rechercher un moyen, permettant les dosages de calcium et magnésium en présence d'aluminium, fer et titane aux teneurs moyennes de ces éléments généralement présentes dans les silicates. Des techniques existent pour le masquage de l'aluminium et du fer par la triéthanolamine[1,2,8,9] et des métaux lourds par le cyanure de potassium[10].

L'action de la triéthanolamine est efficace en milieu fortement alcalin (pH $\geqslant 12$) et convient bien pour le dosage du calcium; en présence de fer la coloration brune formée disparaît lors de l'addition de la solution potassique. Dans le cas du dosage du magnésium la nécessité de travailler à pH 10, pour éviter la précipitation de la magnésie en milieu alcalin plus élevé, diminue considérablement l'effet protecteur de ce réactif. En outre, le fer présent dans le milieu analysé perturbe par son effet oxydant le virage du noir ériochrome T, employé comme indicateur[8].

Le cyanure de potassium forme avec certains cations des groupes analytiques I et II des complexes très stables, mais, pour obtenir le masquage de ces cations, il est nécessaire d'utiliser un excès de réactif, ce qui rend cette technique difficilement utilisable. En effet, d'une part le cyanure en forte concentration influe sur le pH (effet d'hydrolyse) et d'autre part, les complexes cyanurés, étant colorés, peuvent gêner la perception du virage des indicateurs. Enfin, l'inconvénient des manipulations systématiques d'importantes quantités de cyanure de potassium se passe de commentaires.

Pour ces multiples raisons, nous avons été amenés à approfondir ce problème, car les moyens cités ne présentaient qu'une solution partielle dans notre cas.

PARTIE EXPÉRIMENTALE

Nous envisagerons deux cas: celui du calcium en présence de l'aluminium, du fer et du titane et celui de la somme de calcium + magnésium en présence de ces trois éléments.

Dosage direct de calcium

Nous avons, d'abord, vérifié l'action masquante de la triéthanolamine sur des solutions à différentes concentrations d'aluminium, fer et titane, à côté du calcium et déterminé les teneurs limites tolérables de ces trois éléments, soit, respectivement, 50 mg, 50 mg et 5 mg (exprimés en oxydes: Al_2O_3, Fe_2O_3 et TiO_2). Nous avons pu ainsi doser sur des silicates cet alcalino-terreux par le complexon III en présence de murexide (indicateur) et de triéthanolamine (agent masquant). Les résultats de certains de ces essais sont consignés dans le Tableau I.

Toutefois, le virage de la murexide déjà délicat à saisir dans le cas d'un dosage de calcium après séparation préalable de l'aluminium, du fer et du titane, devient encore moins perceptible lorsque la titration est effectuée d'une façon directe. Le mélange d'indicateur composé de murexide et de vert-naphtol B[11] n'est pas plus avantageux.

TABLEAU I

DOSAGES DE CALCIUM ET MAGNÉSIUM PAR COMPLEXOMÉTRIE SUR DES PRODUITS NATURELS

	Après élimination de Fe, Ti, Al		*En présence de Fe, Ti, Al*	
	CaO %	*MgO %*	*CaO %*	*MgO %*
Schiste	2.24	1.52	2.32	1.60
Granit	2.40	0.61	2.52	0.60
Granit	1.04	0.04	1.12	traces
Granit	0.22	1.76	0.20	1.85
Grès	2.35	1.18	2.34	1.20
Argile	0.53	0.42	0.53	0.40
Ciment	63.7		64.00	
Dolomie	35.70	16.17	36.00	16.07
Calcaire	56.00		56.02	traces
Feldspath	0.35	0.08	0.30	traces
Argile marneuse	20.07	1.12	19.85	1.19
Feldspath	2.00	1.34	1.90	1.33
Feldspath	2.24	traces	2.10	traces
Argile marneuse	23.87	1.51	23.21	1.35

Un nouvel indicateur, la calcéine permet d'effectuer de très bons dosages du calcium par le complexon III à pH 12, le virage de la teinte vert-jaune à la teinte rose est beaucoup plus net que celui de la murexide. Toutefois, nous avons constaté, ainsi que l'a fait THOMPSON[12], que la calcéine en présence de triéthanolamine ne vire pas au moment de la fixation des ions Ca^{+2} par l'EDTA. Ce fait a conduit cet auteur à abandonner l'emploi de la calcéine. Nous avons trouvé qu'une addition d'acide tartrique au milieu analytique permettait de percevoir très nettement le virage de cet indicateur. Dans ce cas la teneur limite d'aluminium que l'on peut tolérer dans la solution à analyser se trouve portée à 150 mg, exprimés en oxyde, celles de titane et fer étant respectivement 5 mg et 10 mg (en oxyde de l'élément).

L'acide tartrique donne avec l'aluminium, le fer et le titane des complexes qui sont caractérisés par leur insensibilité vis-à-vis des alcalins. Les solutions potassique ou sodique loin de précipiter les hydroxydes stabilisent les complexes formés dans ce cas.

A titre d'exemple, nous donnons dans les Tableaux II et III des valeurs pour Ca trouvées sur des solutions synthétiques et sur des ciments, suivant le mode opératoire qui sera décrit en annexe.

Dosage du magnésium en présence de Al, Fe et Ti

Nous avons signalé dans l'introduction les difficultés qui se présentent dans le cas du dosage du magnésium, effectué dans un milieu contenant Al, Fe et Ti. Bien entendu, lorsque le calcium accompagne le magnésium, c'est la somme Ca + Mg qui est dosée suivant les conditions opératoires définies pour le magnésium seul. Différentes techniques ont été essayées parmi lesquelles nous citons: la réduction du fer par l'acide ascorbique, le masquage par le cyanure de potassium[1,2,8,10,11], la formation de complexe par l'EDTA à pH 4–4.5 et l'emploi de différents indicateurs[13,14]. Dans tous les cas les résultats trouvés ont été assez décevants.

La seule méthode qui nous a donné des résultats satisfaisants, dans le cas des silicates, a été le dosage du magnésium en présence de triéthanolamine, d'acide tartrique et de noir ériochrome T (indicateur). La présence d'acide tartrique permet d'effectuer le dosage dans une zone de pH élevé. La magnésie ne précipite pas, le fer se trouve complexé, reste en solution et n'entre pas en réaction avec l'EDTA. L'influence de la triéthanolamine en est d'autant plus efficace, l'aluminium, le fer et le titane ne sont plus gênants jusqu'à respectivement 50 mg, 10 mg et 10 mg exprimés en oxydes.

Le mode opératoire de ce dosage se trouve décrit en annexe et quelques résultats sont donnés dans les Tableaux I et IV.

DISCUSSIONS DES RÉSULTATS

Des essais effectués sur des solutions synthétiques et sur des silicates très différents par leur structure minéralogique et leurs compositions tels que schistes, marnes, argiles, feldspaths, kaolins, granits, etc . . . montrent la possibilité d'un dosage direct de calcium en présence d'aluminium, fer et titane. Les résultats trouvés dans ce cas sont très voisins de ceux obtenus par dosage complexométrique après séparation des hydroxydes.

En déterminant directement le calcium sur une partie aliquote de la solution provenant de l'attaque sulfo-fluorhydrique de la matière silico-alumineuse, on supprime très certainement l'erreur possible, due à la perte d'une certaine quantité de cet élément adsorbé sur le précipité colloïdal des hydroxydes d'aluminium, de fer et de titane, obtenu par le procédé classique à l'ammoniaque. D'autre part, on diminue dans le cas d'un dosage direct la quantité d'impuretés introduites par les réactifs employés au cours d'une telle précipitation. Certains dosages à blanc donnent jusqu'à 0.5% de CaO, apportés de la sorte.

Ces quelques considérations formulées pour le calcium sont également valables pour le magnésium, réserve faite toutefois pour le taux de contamination généralement

TABLEAU II

DOSAGE DIRECT DU CALCIUM SUR SOLUTION SYNTHÉTIQUE EN MILIEU TARTRIQUE AVEC LA CALCÉINE (INDICATEUR) EN PRÉSENCE DE Al, Fe ET Ti

Complexon 0.05 M				*CaO mg trouvé*			*Moyenne*
CaO mg	*Al_2O_3 mg*	*Fe_2O_3 mg*	*TiO_2 mg*				
5.32	150			5.32	5.32	5.32	5.32
2.66	70	10	5	2.66	2.66	2.66	2.66
1.33	70	10	5	1.40	1.40	1.40	1.40
0.532	70	10	5	0.56	0.56	0.56	0.56
0.266	70	10	5	non dosable avec complexon 0.05 *M*			

Complexon 0.01 M				*CaO mg trouvé*			*Moyenne*
CaO mg	*Al_2O_3 mg*	*Fe_2O_3 mg*	*TiO_2 mg*				
2.66	70	10	5	2.404	2.52	2.52	2.48
1.33	70	10	5	1.26	1.26	1.28	1.26
0.532	70	10	5	0.61	0.61	0.61	0.61
0.266	70	10	5	0.28	0.28	0.28	0.28
2.66	70	5	2	2.57	2.57	2.57	2.57
1.33	70	5	2	1.28	1.31	1.31	1.306
0.532	70	5	2	0.67	0.61	0.61	0.63
0.266	70	5	2	0.28	0.28	0.28	0.28
2.66	70	2	1	2.604	2.604	2.604	2.60
1.33	70	2	1	1.316	1.316	1.28	1.30
0.532	70	2	1	0.56	0.56	0.56	0.56
0.266	70	2	1	0.28	0.25	0.28	0.27

TABLEAU III

DOSAGE DIRECT DU CALCIUM EN MILIEU TARTRIQUE DANS LES CIMENTS

Echantillons analysés	*CaO %*				
	Gravimétrie	*Complexon III*			
Ciment type A (en présence de SiO_2)		65.90	65.57	65.57	65.90
Ciment type A (après séparation de SiO_2)	65.00	66.10	66.02	66.10	66.10
Ciment type B (en présence de SiO_2)		63.84	63.84	63.84	63.84
Ciment type B (après séparation de SiO_2)	64.00	64.40	64.40	64.40	
Ciment type L (après séparation de SiO_2)	45.30	45.80	45.80	45.80	

bien plus faible apportée par les réactifs pour ce dernier élément. Il est superflu de mettre en évidence les avantages de la rapidité de la méthode. Le gain de temps obtenu par le dosage direct est considérable; il se chiffre par de nombreuses heures de travail. La sensibilité, les limites de détection et l'ordre de grandeur de la précision, restent les mêmes que ceux des analyses complexométriques en général. Les essais comparatifs effectués sur le calcium avec la murexide et la calcéine sont nettement plus favorables pour ce dernier réactif. La netteté du virage obtenu est assez remarquable, aussi bien en absence qu'en présence des éléments ,,gênants": Al, Fe, Ti.

Pour le magnésium, signalons que le virage déjà quelque peu délicat à percevoir en absence des hydroxydes le devient encore plus lors du dosage direct effectué selon la méthode décrite dans ce travail.

TABLEAU IV

DOSAGE DIRECT DE MgO EN MILIEU TARTRIQUE EN PRÉSENCE DE Al, Fe ET Ti

(sur solutions synthétiques)
Complexon 0.05 *M*

MgO mg	*Al_2O_3 mg*	*Fe_2O_3 mg*	*TiO_2 mg*	*MgO mg trouvé*			
8.8	50	10	5	8.8	8.6	8.8	8.8
4.4	50	10	5	4.4	4.4	4.4	4.4
2.2	50	10	5	2.2	2.2	2	2.2
1.1	50	10	5	1	1	1.1	1
0.44	50	10	5	0.43	0.43	0.43	0.43
0.22	50	10	5	0.21	0.21	0.21	0.21

Nous attirons l'attention du lecteur sur cet inconvénient, tout en lui signalant que des études sont en cours pour trouver une amélioration à ce manque de sensibilité. A cet égard, l'*o*-cresolphtaléine complexone semble donner un virage plus net (violet → incolore) que celui observé avec le noir ériochrome T et peut être utilisé à sa place.

CONCLUSION

L'analyse du calcium et du magnésium dans des produits complexes, tels que les silicates, effectuée sur une attaque sulfo-fluorhydrique de la matière au cours de laquelle la silice est eliminée par volatilisation, nécessite la séparation préalable de l'aluminium, du fer, du titane et, éventuellement du manganèse et du chrome, puis, des sels ammoniacaux formés au cours de cette opération.

Différentes techniques examinées en vue de doser le calcium et le magnésium en présence d'aluminium, fer et titane, nous ont donné des résultats partiellement satisfaisants. La méthode trouvée apporte des avantages certains dans le cas du dosage direct du calcium et malgré certains inconvénients constatés pour le dosage du magnésium, réunit de nouvelles conditions d'analyse.

Cette technique est basée sur l'utilisation de l'acide tartrique et de la triéthanolamine (binôme complexifiant), de la calcéine et du noir ériochrome T (indicateurs), et du complexon III (réactif titrant).

ANNEXE

Mode opératoire

Principe

Les sels de Al, Fe et Ti sont masqués par l'acide tartrique et la triéthanolamine et de ce fait, Ca et Mg forment seuls des complexes avec l'EDTA. La fin de ces réactions est décelée par des indicateurs appropriés qui changent de coloration dès la disparition des ions Ca^{+2} et Mg^{+2} de la solution analysée.

Réactifs utilisés

Acide sulfurique, $d = 1.83$; Acide fluorhydrique à 40%; Acide chlorhydrique, $d = 1.19$; Acide tartrique à 2%; Solution d'hydroxyde de potassium environ 4 N: Dissoudre 228 g d'hydroxyde de potassium dans 1000 ml d'eau distillée; Indicateur à base de calcéine: broyer 0.100 g de calcéine dans 100 g de chlorure de sodium; Solution de complexon III (dihydrate du sel disodique de l'acide éthylène diamine tétraacétique) exactement 0.01 M: Peser 3.721 g de complexon III, les dissoudre dans de l'eau distillée, ajuster à 1000 ml; Solution de complexon III, 0.05 M: Peser 18.605 g de complexon III, les dissoudre dans de l'eau distillée ajuster à 1000 ml; Solution exacte à 1 g/l CaO: Peser 1.7846 g de carbonate de calcium, le dissoudre dans de l'eau distillée additionnée de 3 à 5 ml de HCl, $d = 1.19$. Compléter à 1000 ml; Solution à 1 g/l MgO: Peser 6.1160 g de sulfate de magnésium $MgSO_4 \cdot 7\ H_2O$, le dissoudre avec de l'eau distillée, ajuster à 1000 ml. Note: On peut utiliser également le nitrate ou le chlorure de magnésium); Triéthanolamine; Ammoniaque, $d = 0.92$; Noir ériochrome T; Chlorure d'ammonium; Indicateur à base de noir ériochrome T: broyer 0.300 g de noir ériochrome avec 100 g de NH_4Cl.

Dosage du calcium

Pratique du dosage

A la solution chlorhydrique à doser qui doit être amenée à un volume d'environ 50 ml et contenir plus de 0.30 mg de CaO, ajouter: 10 ml de solution d'acide tartrique à 2%; 10 ml d'hydroxyde de potassium et environ 100 mg d'indicateur calcéine. La solution prend une coloration jaune-vert.

Titrer avec une solution étalon de complexon III, 0.01 M ou 0.05 M suivant les quantités de calcium à doser, jusqu'à virage de la coloration au *rose stable*.

Remarques

Dans le cas d'une faible teneur en Ca (moins de 0.30 mg dans la solution à doser), il est nécessaire d'ajouter un certain volume de solution à 1 g/l CaO qui sera déduit du résultat obtenu.

Moins il y a de Ti et Fe dans la solution plus le virage est net; il est bon par conséquent de faire en sorte que les quantités présentes de ces deux éléments soient inférieures respectivement à 5 mg (Ti) et 10 mg (Fe) dans la solution à doser.

Calcul

1 ml de solution de complexon 0.05 *M* correspond à 2.804 mg de CaO. 1 ml de solution de complexon 0.01 *M* correspond à 0.561 mg de CaO.

Dosage de l'ensemble calcium et magnésium

Pratique du dosage

A la solution chlorhydrique à doser qui doit occuper un volume d'environ 50 ml et contenir plus de 1 mg de MgO, ajouter: 10 ml de solution d'acide tartrique à 2%; 10 à 15 ml de triéthanolamine; mélanger avec soin et ajouter encore, 10 ml d'ammoniaque et environ 1 g d'indicateur noir ériochrome T. La solution prend une coloration rouge violet. Titrer avec le complexon 0.05 *M* jusqu'à virage au bleu violet. Les gouttes de complexon tombant dans la solution y forment des filets bleus au début du dosage, puis deviennent blanches lorsque le magnésium est complexé.

Remarques

Il est conseillé de réaliser le dosage rapidement à l'aide d'une burette au 1/20 de ml, car on utilise afin de bien percevoir le virage le complexon 0.05 *M* dont chaque goutte correspond à une quantité importante de MgO. Dans le cas de faibles quantités de MgO (< 5 mg), il est nécessaire d'ajouter 5 ml de solution à 1 g/l de MgO, et d'en tenir compte dans le calcul.

Calcul de la teneur en magnésium

1 ml de complexon 0.05 *M* correspond à 2.016 mg de MgO.

Application à l'analyse des silicates

Attaque du produit

On opère sur le produit broyé, passé au tamis 21 AFNOR (mailles de 0.1 mm) et séché à 110°, jusqu'à poids constant. 1 g environ est pesé sur une balance de précision au 1/10 de mg, dans une capsule de platine et soumis à l'attaque acide HF/H_2SO_4 à la température du bain de sable: 240° environ. On répète 3 fois l'addition de HF puis on reprend le résidu sec par de l'eau distillée et 10 ml de HCl dans un bécher. On porte à l'ébullition jusqu'à dissolution complète, puis après refroidissement, on introduit en fiole jaugée de 250 ml et on ajuste au volume avec de l'eau distillée. Les dosages décrits sont effectués sur des prises aliquotes de 25 ml, soit sur 1/10 de la prise d'essai.

Pratique du dosage

Mode opératoire décrit pages 524 et 525.

Remarques

Il est possible d'opérer ces dosages sur les solutions issues d'attaques au carbonate de l'échantillon, après l'insolubilisation de la silice par HCl ou HCl–gélatine.

RÉSUMÉ

Les dosages de calcium et de magnésium à l'aide du sel disodique de l'acide éthylène-diamine tétraacétique dans des produits tels que les silicates naturels (argiles, kaolins, feldspaths, marnes, etc. . . .) ou complexes (émaux, frittes) comme ils étaient pratiqués avant cette étude, étaient relativement longs car ils nécessitaient d'une part la séparation préalable de l'aluminium, fer, titane et autres métaux lourds, d'autre part, l'élimination des sels ammoniacaux formés au cours de cette opération. Dans ce travail plusieurs méthodes ont été examinées en vue de doser le calcium et le magnésium en présence de fer, titane et aluminium. Elles diffèrent, entre elles, surtout par le choix des réactifs destinés à complexifier les ions gênants. La méthode trouvée donne des résultats tout à fait comparables à ceux obtenus après séparation des éléments Al, Fe et Ti. Elle est basée sur l'utilisation de l'acide tartrique et de la triéthanolamine (binome complexifiant), de la calcéine et du noir ériochrome T (indicateur) et du complexon III (réactif titrant). Le mode opératoire détaillé de cette technique est donné en annexe.

SUMMARY

Description of a volumetric method for the determination of Ca and Mg in the presence of Al, Fe and Ti by titration with Complexon III; tartaric acid and triethanolamine are present. Calcein and eriochrome black are used as indicators.

ZUSAMMENFASSUNG

Beschreibung einer volumetrischen Methode zur Bestimmung von Ca und Mg neben Al, Fe und Ti durch Titration mit Komplexon III in Gegenwart von Weinsäure und Triäthanolamin und mit Calcein und Eriochromschwarz als Indikatoren.

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DIALLYLDITHIOCARBAMIDOHYDRAZINE (DALZIN) AS AN ANALYTICAL REAGENT

DETERMINATION OF PALLADIUM AND ITS SEPARATION FROM NICKEL, ZINC AND COPPER

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Dalzin has been used for the determination and separation of a number of metals[1]. Further investigation has shown that palladium can be quantitatively precipitated from hot solutions by Dalzin at pH 3.1–4.5, while most of the common ions and other platinum metals remain in solution. Copper, mercury and silver interfere, but the interference of copper can be eliminated by complexing with EDTA and precipitating palladium at a pH below 4.5. Nickel and zinc can be determined in the filtrate after raising the pH as usual.

EXPERIMENTAL

Chemicals used were all of A.R. quality. A palladium solution was prepared from palladium chloride (Johnson and Matthey) and standardized gravimetrically as palladium dimethylglyoxime. pH measurements were made with Philips pH meter.

Composition of palladium complex

Palladium was precipitated at pH *ca.* 4 by the method given below and the precipitate was dried at 105° to constant weight. A weighed quantity was decomposed with aqua regia and evaporated several times with concentrated hydrochloric acid and the residue was taken up with this acid and diluted to 100 ml. Palladium in the solution was determined by the dimethylglyoxime method. The complex was found to have the composition $Pd(C_8H_{12}N_4S_2)\ H_2O$ (Pd. calc. 30.22%, found 29.93%).

Determination of palladium

The palladium chloride solution (30–60 mg Pd) was neutralised with ammonia and diluted to about 100 ml and the pH was adjusted with a freshly prepared solution of citric acid. The solution was heated on a water-bath and 25 ml of a hot alcoholic 1.0% solution of the reagent was added with constant stirring. The brick-red precipitate was allowed to settle and was filtered through a weighed sintered glass crucible. Filtrates were kept for pH determinations. The precipitate was washed with hot water and acetone, dried at 105° and weighed (Pd factor = 0.3022). The results are shown in Table I.

TABLE I

Weight of Pd compound g	*Pd found* g	*Pd taken* g	*pH*
0.0983	0.02971	0.03024	2.2
0.1177	0.03557	0.03629	2.7
0.1198	0.03620	0.03629	3.1
0.1998	0.06040	0.06049	3.5
0.1594	0.04818	0.04839	4.0
0.1795	0.05425	0.05444	4.5
0.1180	0.03567	0.03629	4.8
0.1775	0.05364	0.05444	5.1

Separation of Pd–Ni and Pd–Zn

A solution of palladium containing nickel or zinc was treated as in the above procedure. Nickel or zinc was estimated in the filtrate with the same reagent as previously described[1]. The results are shown in Table II.

TABLE II

Pd compound g	*Pd found* g	*Pd taken* g	*Ni found* g	*Ni taken* g	*Zn found* g	*Zn taken*
0.0998	0.03006	0.03024	0.07791	0.07801		
0.1201	0.03629	0.03629	0.02922	0.02925		
0.1396	0.04219	0.04234	0.05832	0.05850		
0.1596	0.04825	0.04839	0.04335	0.04388		
0.1795	0.05425	0.05444			0.04158	0.04175
0.1797	0.05431	0.05444			0.02487	0.02505
0.1001	0.03026	0.03024			0.04168	0.04175
0.1003	0.03032	0.03024			0.06231	0.06212

TABLE III

Wt. of foreign ion mg		*Wt. of Pd compound* g	*Pd found* g	*Pd taken* g
Cu	50	0.1179	0.03562	0.03629
	100	0.1200	0.03626	0.03629
Be	50	0.1595	0.04828	0.04839
	100	0.1806	0.05458	0.05444
Mg	50	0.1398	0.04225	0.04234
	50	0.1596	0.04828	0.04839
Ca	100	0.1795	0.05425	0.05444
	200	0.1003	0.03032	0.03024
Ba	100	0.1003	0.03032	0.03024
	200	0.1003	0.03032	0.03024
Sr	100	0.1004	0.03034	0.03035
	200	0.1005	0.03037	0.03038
Th	25	0.1795	0.05425	0.05444
	50	0.1795	0.05425	0.05444
Ce	25	0.1794	0.05423	0.05444
	50	0.1803	0.05446	0.05446
Mn	25	0.1808	0.05462	0.05444
	50	0.1792	0.05416	0.05444

Determination in presence of various ions

Solutions of palladium containing other ions were treated as above. Copper was kept in solution with the aid of EDTA. The ions studied are given in Table III.

SUMMARY

Palladium is precipitated quantitatively by Dalzin at pH *ca.* 4, and can be determined. It is separated from nickel and zinc which can be determined in the filtrate with the same reagent.

RÉSUMÉ

Les auteurs ont mis au point une méthode de dosage gravimétrique du palladium au moyen de diallyldithiocarbamidohydrazine ("Dalzine"); il est possible d'effectuer une séparation d'avec Ni, Zn et Cu.

ZUSAMMENFASSUNG

Beschreibung einer gravimetrischen Bestimmung von Palladium mit Hilfe von Diallyldithiocarbamidohydrazin mit Angaben über Trennungen von anderen Metallen.

REFERENCE

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THE GRAVIMETRIC DETERMINATION OF CADMIUM WITH THE SODIUM SALT OF 1-PHENYL-TETRAZOLINE-5-THIONE

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The acid, 1-phenyl-tetrazoline-5-thione, has the structure indicated in Fig. 1. Structure II has been proposed as the enolized form of structure I[1,2]. Infrared absorption data, however, have shown that I is the preferred structure of the compound and that the thiol form is not present[3]. Investigations by Lieber* and his associates have shown that the 1-tetrazoline thionyl group is electron withdrawing and that the hydrogen residing on the nitrogen atom at position four of the heterocyclic ring is acidic. The

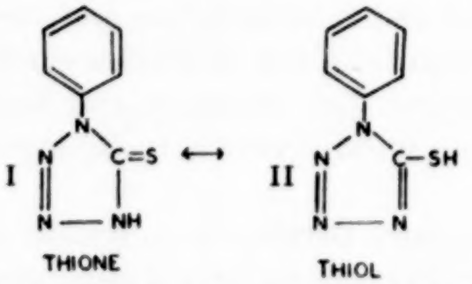

Fig. 1. 1-Phenyl-tetrazoline-5-thione.

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* Our attention was called to this compound by Professor Eugene Lieber of Roosevelt University.

pK_a of this hydrogen is 3.65 at 25°. It is completely dissociated in 0.1 N sodium hydroxide and even in a buffered solution of pH 7.5, the dissociation is nearly complete[4]. Thus the compound readily forms salts. The sodium salt has been used as the reagent in our studies.

Reagent preparation

The 1-phenyl-tetrazoline-5-thione is easily prepared by refluxing a mixture of phenyl isothiocyanate and sodium azide, at a mole ratio of 1 : 1.5, in water (100 ml of water per 0.1 mole isothiocyanate) for four hours. The resulting mixture is extracted with ether to remove the unreacted phenyl isothiocyanate and is then acidified with hydrochloric acid, precipitating the tetrazoline compound from solution. The product is collected on filter paper, washed with cold water and recrystallized from hot water, giving white needles melting at 149°–150°[5].

The sodium salt of the tetrazoline compound is prepared by dissolving the acid form in 20% sodium hydroxide solution. The resulting solution is evaporated to dryness, and the sodium salt is extracted with absolute ethanol which will not dissolve the sodium carbonate formed from the excess sodium hydroxide. The alcoholic solution of the sodium salt is then carefully evaporated to dryness and the solid material is extracted with water. The final form of the sodium salt is obtained from this solution by evaporating until the needles of the sodium salt form when the solution is chilled. The second extraction is used to separate any organic impurities which may be present after the ethanol extraction. The sodium salt obtained above is very soluble in water. Solutions have been made which contain approximately 64 g solute per 100 ml solution.

Study of the reagent

In using the reagent in the precipitation of metal ions, the control of the pH of the solution is important. Below pH 5, the water insoluble acid form of the reagent is regenerated. When the precipitation is attempted in very basic solutions, there occurs some decomposition of the reagent which yields sulfide-like materials.

Qualitative studies employing the sodium salt of the reagent gave precipitates with cobalt, nickel, zinc, silver, cadmium, mercury and lead. All of these precipitates are white in color with the exception of cobalt which, at first, yields a bluish-white precipitate which turns intensely blue upon standing. The rate of this color change is analogous to a clock reaction and is temperature and concentration dependent. No precipitation was observed with the alkali or alkaline earth metals. Precipitates were obtained with chromium, copper, tin, antimony and bismuth. It was determined, however, that these latter precipitates were actually regenerated reagent in various stages of decomposition.

Sensitivity determinations were performed on cobalt, zinc, nickel, cadmium and lead. Cadmium, lead and zinc gave precipitates at concentrations of 1, 2, and 6 p.p.m. respectively.

Since there are few good weighing forms for cadmium, the high sensitivity of the cadmium precipitation gave promise for a new weighing form for the gravimetric determination of cadmium. The cadmium precipitate which is a white crystalline material, has been found by analysis to contain a 2 : 1 mole ratio of the tetrazole to cadmium.

The molecular weight of the compound, which contains 24.08% cadmium, is 466.85. The compound has a molar solubility of $2.0 \cdot 10^{-5}$ moles per liter at 25° and a solubility product of $3.03 \cdot 10^{-14}$ at this temperature. The cadmium precipitate may be readily dried at 110°.

The gravimetric determination of cadmium was carried out using aqueous 5% and saturated solutions of the reagent. The amount of cadmium determined varied from 1–40 mg. A standard cadmium solution was prepared from reagent grade $Cd(NO_3)_2$ and standardization by electrodeposition indicated a concentration of 2.039 mg cadmium per ml. This solution was used for the larger cadmium samples and was diluted for the smaller samples. The volume of the sample solution prior to precipitation was adjusted to approximately 50 ml.

The reagent was added dropwise to the cadmium solutions which were heated to just below their boiling point. After the addition of a few drops of the reagent, the solutions were stirred briefly and then allowed to stand until the precipitate, which started to form immediately, was noticed to form aggregates. The remaining portion of the reagent solution was then added with stirring. The samples were filtered using medium porosity porcelain filtering crucibles. Approximately 125 ml distilled water was used to wash and transfer the precipitates, which were dried at 110° until constant weight was attained. The results of these determinations are summarized in Tables I

TABLE I

CADMIUM PRECIPITATION WITH SATURATED REAGENT SOLUTION

mg Cd taken	*mg Cd recovered*	*Average recovery*	*Average deviation*
40.8	40.5	40.6	0.6/1000
40.8	40.6		
40.8	40.6		
40.8	40.6		
20.4	20.1	20.3	6/1000
20.4	20.2		
20.4	20.2		
20.4	20.4		
20.4	20.4		
5.1	4.8	4.9	24/1000
5.1	4.8		
5.1	5.0		
5.1	5.0		
5.1	5.1		
1.0	0.8	0.9	92/1000
1.0	0.8		
1.0	0.8		
1.0	0.9		
1.0	0.9		
1.0	1.0		
1.0	1.0		
1.0	1.0		
1.0	1.0		
1.0	1.0		
1.0	1.0		
1.0	1.1		

and II. A series of experiments were carried out using 10% ethanol to reduce the solubility of the precipitate. These results are summarized in Table II. Coprecipitation studies were made with manganese and magnesium since these elements are often found in cadmium alloys. The results in Table III indicate negligible coprecipitation.

DISCUSSION

In the comparison of Tables I and II, it is seen that the quantitative recovery of cadmium is very similar with both the saturated and 5% solutions of the reagent. The results obtained when using the saturated solution generally show a higher degree of accuracy and better precision, especially with the larger cadmium samples. Also in Table II, there are results of the precipitation of cadmium employing ethanol to depress the solubility of the precipitate. The improvement of the accuracy is such that the added effort is not warranted. The presence of ethanol tends to make the transfer of the precipitate more difficult and time-consuming.

Preliminary investigations have indicated that this reagent may also be useful for the determination of lead and zinc.

TABLE II

CADMIUM PRECIPITATION WITH 5% REAGENT SOLUTION

mg Cd taken	*mg Cd recovered*	*Average recovery*	*Average deviation*
40.8	40.1	40.4	4/1000
40.8	40.3		
40.8	40.4		
40.8	40.6		
20.4	19.8	20.3	14/1000
20.4	20.5		
20.4	20.5		
20.4	20.5		
5.1	4.5	4.8	21/1000
5.1	4.8		
5.1	4.8		
5.1	4.9		
1.0	0.7	0.9	100/1000
1.0	0.8		
1.0	0.8		
1.0	0.8		
1.0	0.9		
1.0	1.0		
1.0	1.0		
1.0[a]	0.7	1.0	150/1000
1.0[a]	0.9		
1.0[a]	1.1		
1.0[a]	1.1		
1.0[b]	0.8	0.9	50/1000
1.0[b]	0.9		
1.0[b]	0.9		
1.0[b]	1.0		

[a] Precipitate washed with 10% EtOH solution.

[b] Cadmium precipitated in and washed with 10% EtOH solution.

TABLE III

CADMIUM PRECIPITATION IN PRESENCE OF MANGANESE AND MAGNESIUM WITH SATURATED REAGENT SOLUTION

mg Cd taken	*mg Mn taken*	*mg Mg taken*	*mg Cd recovered*	*Average mg Cd recovered*
20.4	5.0	none	20.3	20.4
20.4	5.0	none	20.4	
20.4	10.0	none	20.4	20.4
20.4	10.0	none	20.4	
20.4	none	5.0	20.3	20.4
20.4	none	5.0	20.4	
20.4	none	10.0	20.3	20.4
20.4	none	10.0	20.4	
20.4	5.0	5.0	20.3	20.4
20.4	5.0	5.0	20.5	
20.4	none	none	20.3	20.4
20.4	none	none	20.3	
20.4	none	none	20.4	
20.4	none	none	20.5	

SUMMARY

The use of the sodium salt of 1-phenyl-tetrazoline-5-thione provides a good method for the quantitative determination of cadmium, yielding a crystalline precipitate which is easily filtered and brought to constant weight. The precision of the determination is fair and the accuracy is generally withing 0.2 mg. The main limitation of the reagent is that it is not specific in its action and it might be necessary to effect a prior separation since cadmium is often found to be alloyed with lead and zinc.

RÉSUMÉ

Le sel de sodium de la phényl-1-tétrazoline-thione-5 peut être utilisé comme réactif pour le dosage gravimétrique du cadmium. Cependant cette méthode est peu spécifique et une séparation préalable est souvent nécessaire.

ZUSAMMENFASSUNG

Das Natriumsalz des 1-Phenyl-tetrazolin-5-thions kann zur gravimetrischen Bestimmung von Cadmium verwendet werden. Da das Reagenz wenig spezifisch ist, müssen störende Elemente, vor allem Blei und Zink, vorher entfernt werden.

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AN IMPROVED TITRIMETRIC METHOD FOR DETERMINING SULPHUR TRIOXIDE IN FLUE GAS

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INTRODUCTION

The presence of a few parts per million of sulphur trioxide in flue gas has caused serious problems due to the deposition of sulphuric acid on the low temperature parts of oil-fired boilers. The concentration of sulphur trioxide is a measure of the corrosive nature of the flue gas and its determination is therefore important.

The measurement of sulphur trioxide concentrations in the range 0–50 p.p.m. v/v in the presence of a large excess (2,000–3,000 p.p.m. v/v) of sulphur dioxide[1–3] is usually carried out in two stages:

(*1*) Quantitative absorption of the sulphur trioxide from a sample of flue gas in an aqueous solution of isopropanol, which inhibits oxidation of sulphur dioxide.

(*2*) Determination of microgram quantities of sulphur trioxide in the aqueous isopropanol.

In most techniques described in the literature[1,3–5] sulphate in the aqueous isopropanol has been determined turbidimetrically; this technique possesses limited sensitivity and precision, and is rather time-consuming.

A titrimetric method for determining sulphate[6] was applied by SEIDMAN[7] to the measurement of sulphur trioxide in flue gas: the lower limit for the determination was 10 p.p.m. v/v of sulphur trioxide in the flue gas. For application in modern power stations, it is desirable that the lower limit should be not more than 0.5 p.p.m. SO_3 v/v, corresponding to about 0.25 p.p.m. SO_3 v/v in the isopropanol solution*.

This paper presents the results of work on a titrimetric determination for flue gas analysis and compares the results with others obtained using an established turbidimetric technique[3].

EXPERIMENTAL

In alcoholic solution, barium ions form a complex with Thoron (the sodium salt of 1-(*o*-arseno-phenyl-azo)-2-naphthol-3 : 6 disulphonic acid). Thoron in aqueous alcoholic solution is yellow; the barium complex has a peak of optical absorption at 550 mμ, and appears pink. In this method of analysis, Thoron is added to the solution of sulphate which is then titrated with barium perchlorate in 4 : 1 isopropanol : water to a change of colour from yellow to pink.

It was found by visual observation that the most dilute titrant which gave a reasonably sharp end-point was 0.0025 *M*. At this concentration the end-point could always be determined to within 1 drop (0.02 ml) of titrant (equivalent to 4 μg of SO_3) when the titration was carried out in diffused sunlight. There was no gain in precision on further dilution, as the end-point became less distinct. When an "EEL" photoelectric indicator was used to observe the end-point the concentration of the titrant could be reduced to 0.0005 *M*, and the precision of the method was increased at the lower limit of its range. It was possible by this means to decrease the limit of detection to 2 μg SO_3. This is equivalent to about 0.1 p.p.m. v/v of SO_3 in the sampled gas if a 50-ml aliquot of the sample solution is titrated.

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* Using the C.E.R.L. absorption apparatus[3], flue gas is sampled at 1.0 l/min for about 15 min. The sulphur trioxide is absorbed in a total of 100 ml of aqueous isopropanol.

The interference of sulphur dioxide reported by FRITZ AND YANNAMURA[6] was investigated. Different quantities of sulphate, as sulphuric acid, in 4 : 1 isopropanol : water containing 60 μg/ml of SO_2 were titrated with 0.0025 *M* barium perchlorate*. A graph relating the volume of titrant and the quantity of sulphate added gave a straight line with a small positive intercept on the titrant axis. This "blank" was shown by means of turbidimetric determinations to be equivalent to the small amount of sulphate in the sulphur dioxide solution; there was no interference by sulphur dioxide at the concentration investigated.

The apparent pH of the synthetic solutions and of samples obtained from flue gas was between 3.5 and 4.0 (indicated by a glass electrode). This is within the range of apparent pH (2.5–4.0) stated by FRITZ AND YANNAMURA[6] to be necessary for the end-point to be visible, therefore no adjustment was necessary.

The precision of the method was determined at three levels of sulphate concentration in the presence of 60 μg/ml of dissolved sulphur dioxide, using the technique described in the Appendix.

The results are compared in Table I with those obtained by the turbidimetric method[3]. The lowest concentration quoted was determined using 0.0005 *M* titrant and a photometric end-point indicator.

TABLE I

PRECISION OF TITRIMETRIC AND TURBIDIMETRIC METHODS

Quantity of sulphate taken, μg SO_4	*Concentration in solution, μg SO_4/ml*	*Equivalent concentration in flue gas, p.p.m. SO_3 v/v*	*Titrimetric method (see Appendix)*		*Turbidimetric method[a]*	
			Number of determinations	*Standard deviation, μg SO_4[a]*	*Number of determinations*	*Standard deviation, μg SO_4*
500	25.0	46.7	12	2.0	9	9.0
250	12.5	23.4	—	—	10	5.0
200	10.0	18.7	12	2.0	—	—
50.0	2.5	4.7	12	2.0	10	2.0
8.00	0.16	0.3	10	0.6	—	—

[a] Standard deviation of the results of single determinations about the mean value.

CONCLUSION

The titrimetric method is quicker, more precise, and more sensitive than the turbidimetric method, which it would replace with advantage; it requires less manipulation and the reagents used are stable over long periods. The titrimetric procedure could be used to complete the flue gas analysis at the sampling site and is suitable for routine application to industrial plant.

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* Sample solutions from the absorption apparatus usually contain about 30 μg/ml of [illegible].

APPENDIX

Titrimetric method for determining sulphur trioxide in flue gas

Reagents

Barium perchlorate, 0.0025 *M*: Dissolve about 0.84 g of anhydrous barium perchlorate in 1000 ml of 4 : 1 isopropanol : water. Adjust the apparent pH of the solution to between 2.5 and 4.0 by adding perchloric acid. Standardise the solution by titrating with standard sulphuric acid using the procedure described below.

Thoron indicator, 0.04%: Dissolve 0.04 g Thoron in 100 ml of distilled water.

Sulphuric acid, 0.00125 *N*: Prepare from a gravimetrically standardised solution of sulphuric acid in water, so that the resulting solution is 4 : 1 isopropanol : water. 1 ml of this solution is equivalent to 50.0 μg of sulphur trioxide.

Procedure

These instructions are for the analysis of the 4 : 1 isopropanol : water solution from the absorption apparatus[3]. Transfer to a conical flask a convenient aliquot (10–50 ml) of the solution containing preferably between 50 μg and 500 μg of SO_3. Add 5 drops of the indicator solution for each 20 ml of the test solution. Titrate with the barium perchlorate solution to the appearance of a pink colour. The end-point is most easily seen in diffused sunlight.

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SUMMARY

The titration of sulphate in 4 : 1 isopropanol : water by barium perchlorate to the colour change of Thoron has been applied to the determination of low concentrations of sulphur trioxide (0–50 p.p.m.) in flue gas containing a large excess of sulphur dioxide (2,000–3,000 p.p.m.). The lower visual limit of the end-point was attained using 0.0025 *M* titrant: in determinations of between 50 μg and 500 μg SO_3 the standard deviation of the results was 2 μg SO_3. The range of application of the method was further extended by observing the end-point photometrically; 0.0005 *M* titrant gave a standard deviation of 0.6 μg in determinations of 8 μg SO_3. No interference was given by dissolved sulphur dioxide at concentrations up to 60 μg/ml, that is, twice the usual maximum. The improved titrimetric procedure is more precise and more sensitive than the turbidimetric methods previously used.

RÉSUMÉ

Le titrage des sulfates, en milieu isopropanol–eau (4 : 1) par le perchlorate de baryum, en présence de thoron comme indicateur, a été appliqué au dosage de l'anhydride sulfurique en faibles teneurs (0–50 p.p.m. SO_3) dans des gaz de cheminées, renfermant un gros excès d'anhydride sulfureux (2000 à 3000 p.p.m.). Cette méthode titrimétrique est plus précise et plus sensible que les méthodes turbidimétriques utilisées jusqu'à présent.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung kleiner Mengen Schwefeltrioxyd neben grossen Mengen Schwefeldioxyd in Abgasen. Die in wasserhaltigem Isopropanol gebildete Schwefelsäure wird mit Bariumperchloratlösung in Gegenwart von Thoron als Indikator titriert. Die Endpunktsbestimmung kann visuell oder photometrisch erfolgen. Die beschriebene Methode ist genauer als das nephelometrische Verfahren.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES. IX*

CLÉMENT DUVAL

avec la collaboration technique de

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(Reçu le 5 juillet 1960)

Poursuivant l'étude des substances utilisables comme étalons, nous présentons les 12 corps suivants: bromure de potassium, carbonate de guanidine, acétate de cadmium, anhydride phtalique, acide *o*-phtalique, sulfate de lanthane, citrate de lithium, sulfate de cobalt, sulfate de magnésium, acide malonique, acide succinique et sulfate de potassium.

Toutes ces substances ont été chauffées sur une thermobalance à enregistrement photographique, avec échauffement linéaire de 300° par heure et avec des poids de substance de l'ordre de 200 mg. Les spectres infrarouges ont été réalisés sur poudre, entre 6 et 15 μ, sur le spectromètre Perkin-Elmer 21, avec optique de chlorure de sodium.

Bromure de potassium

Ce sel est toujours sec et anhydre. Son poids ne change pas jusqu'à 800°; la droite de thermolyse n'est pas reproduite.

Il ne donne évidemment pas de spectre infrarouge dans la région étudiée.

Carbonate de guanidinium

Le carbonate de guanidinium est anhydre et stable au moins jusqu'à 150°; après quoi, la décomposition se fait en trois temps avec libération complète du creuset (Fig. 1).

Le spectre infrarouge a fourni trois bandes fortes pour 1662, 1545 et 1392 cm^{-1}, relatives au groupement C=NH et au groupement NH_2, ainsi que la bande forte caractéristique du groupement CO_3 à 880 cm^{-1}.

Acétate de cadmium

Le produit qui nous a servi contenait deux molécules d'eau qu'il a perdues entre 63 et 190° (Fig. 2). Un palier relatif à l'acétate anhydre s'étend alors jusqu'à 286°; la décomposition se produit brusquement et le palier de l'oxyde CdO commence dès 344°.

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* Pour le huitième mémoire de cette série, voir *Anal. Chim. Acta*, 23 (1960) 257.

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Le spectre infrarouge présente les bandes suivantes, communes à la plupart des acétates: 1640 (f), 1554 (TF), 1418 (TF), 1345 (aF), 1046 (aF), 1020 (aF), 945 (aF) cm^{-1}.

Anhydride phtalique

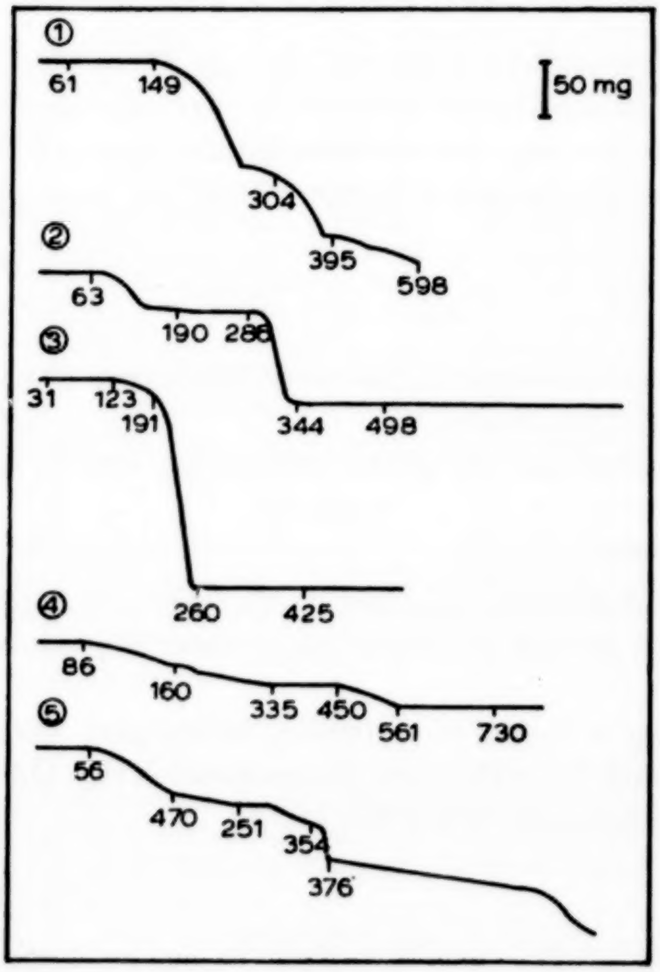
Ce corps se montre bien sec et anhydre et reste stable jusque vers 123°. Il se sublime alors rapidement et le creuset est vide à 260° (Fig. 3).

Le spectre infrarouge présente les bandes suivantes: 1900 (aF), 1843 (F), 1784 (aF), 1731 (F), 1598 (aF), 1471 (F), 1388 (aF), 1363 (F), 1335 (aF), 1283 (aF), 1254 (F), 1243 (f), 1211 (f), 1174 (aF), 1105 (F), 1067 (aF), 1006 (F), 902 (TF), 886 (f), 837 (F), 798 (F), 731 (f), 710 (TF), 676 (F) cm^{-1}.

Acide o-phtalique

La courbe représentative de thermolyse est identique quant à la forme à celle de l'anhydride. Cet acide est sec et stable jusqu'à 187°; après quoi il se déshydrate et se sublime et le creuset est complètement vide à 279°.

Nous avons enregistré le spectre infrarouge qui présente les maxima d'absorption suivants: 1685 (TF), 1587 (aF), 1493 (aF), 1403 (F), 1304 (f), 1281 (F), 1270 (f), 1070 (aF), 1003 (f), 923 (f), 903 (aF), 828 (f), 797 (aF), 737 (aF), 690 (f), 672 (aF) cm^{-1}.



Figs. 1-5.

Sulfate de lanthane

Le sulfate à 8 molécules d'eau que nous avons utilisé est stable jusqu'à 86°. Il donne naissance de 338 à 450° à un palier horizontal correspondant sans doute à un mélange.

Le produit anhydre $La_2(SO_4)_3$ apparaît à 560°; il est préférable de le peser plutôt que le corps de départ (Fig. 4).

Le spectre infrarouge permet de mesurer les bandes de fréquences: 1621 (F), 1420 (F), 1140 (F), 1098 (aF), 1080 (aF), 984 (aF), 657 (aF) cm^{-1}.

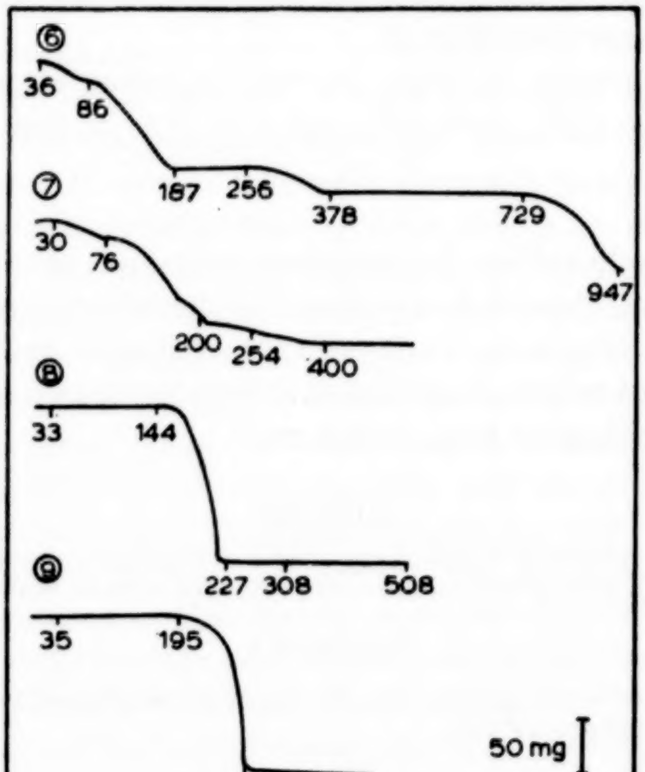
Citrate de lithium

Le produit de départ contient 4 molécules d'eau et il conserve son état d'hydratation jusqu'à 56°; il devient anhydre vers 251° puis se décompose progressivement en abandonnant, au-dessus de 930°, de l'oxyde de lithium plus ou moins carbonaté (Fig. 5).

Nous observons sur le spectre infrarouge les bandes de fréquences suivantes: 1689 (aF), 1595 (TF), 1423 (aF), 1402 (aF), 1388 (aF), 1282 (aF), 1253 (aF), 1110 (aF), 1087 (aF), 1035 (aF), 947 (f), 903 (F), 834 (F) cm^{-1}.

Sulfate de cobalt

Le sulfate de cobalt commercial a été recristallisé une fois dans l'eau; le calcul en donne 7 molécules d'eau. Cet heptahydrate n'est pas stable; déjà, il perd du poids dès 36°; le palier de l'hexahydrate n'est pas nettement marqué et entre 187 et 256° s'étend un autre palier légèrement oblique correspondant assurément à un mélange.



Figs. 6-9.

La déshydratation est achevée à 378° et le palier du sulfate anhydre s'étend jusqu'à 730°. C'est évidemment sous cette forme que l'on obtient les résultats les plus sûrs en vue d'une pesée de précision. Au-dessus de cette température l'anhydride sulfurique se dégage en se dissociant et, vers 950°, on aboutit à l'oxyde Co_3O_4 (Fig. 6).

Le spectre d'absorption infrarouge présente trois bandes fortes pour 1087 et 983 cm^{-1} correspondant au groupement SO_4 et 1634 cm^{-1} relative aux bandes habituelles de l'eau.

Sulfate de magnésium

Ce sel, sorti du flacon, présente 7 molécules d'eau qu'il ne conserve que jusque vers 36°. Il n'y a pas, au cours de la dissociation, de palier très net pour les différents hydrates, avec notre vitesse de chauffe (Fig. 7), c'est pourquoi nous recommandons de porter le corps au-dessus de 400° pour obtenir le sulfate anhydre.

Le spectre d'absorption infrarouge est tout à fait identique à celui du sulfate de cobalt, avec les bandes fortes de 1643, 1084 et 983 cm^{-1}.

Acide malonique

Ce corps est stable et anhydre jusqu'à 144°. Il se décompose alors rapidement jusqu'à 227° et le creuset est débarrassé des dernières traces de carbone vers 420° (Fig. 8).

Le spectre enregistré présente les bandes caractéristiques suivantes: 1735 (f), 1703 (aF), 1437 (f), 1416 (F), 1397 (aF), 1387 (f), 1312 (F), 1257 (aF), 1217 (TF), 1172 (TF), 960 (f), 932 (f), 917 (F), 897 (tf), 769 (TF), 654 (TF) cm^{-1}.

Acide succinique

L'acide succinique se présente également anhydre et est stable jusqu'à 195°. Il se produit alors une brusque décomposition jusque vers 313° et à partir de 449° le creuset est complètement vide (Fig. 9).

Dans le spectre infrarouge, on relève les bandes suivantes: 1689 (TF), 1416 (TF), 1323 (f), 1306 (F), 1200 (TF), 1175 (aF), 918 (aF), 890 (f), 802 (F) cm^{-1}.

Sulfate de potassium

Nous avons chauffé du sulfate de potassium provenant de différents flacons; tous ont perdu au maximum, 1/200 de leur poids en les chauffant jusque vers 800°. On peut, sans doute, attribuer cette perte à une petite trace d'acide sulfurique occlus.

Le spectre d'absorption infrarouge présente bien les deux bandes fortes correspondant au groupement SO_4 pour 1115 et 981 cm^{-1}.

RÉSUMÉ

Cette neuvième étude a porté sur la stabilité thermique et l'enregistrement du spectre d'absorption infrarouge, entre 6 et 15 μ pour douze substances proposées comme étalons en chimie analytique.

SUMMARY

A report is given of the infra-red spectra and the thermal stability of twelve substances that are used as standards in chemical analysis.

ZUSAMMENFASSUNG

Es werden die UR-Spektren sowie das thermische Verhalten von zwölf Substanzen, die in der analytischen Chemie als Standardsubstanzen verwendet werden, beschrieben.

IMPURITY DETERMINATION BY THERMAL ANALYSIS

I. THE MELTING CURVE OF A GRADUALLY FROZEN SAMPLE

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INTRODUCTION

The interpretation of melting curves is based on the assumption that thermodynamic equilibrium prevails throughout the solid and the liquid phase during the determination of the curve. A number of experimental circumstances resulting in insufficient thermodynamic equilibrium have been discussed in a previous paper[1]. Attention has been paid to the limited mass transfer in the liquid and it has been shown that its influence may be neglected under suitable experimental conditions[2].

Thus far, no attention has been paid to the influence of the rate of mass transfer *in the solid*. As is obvious a limited rate of mass transfer in the solid has no effect on the attainment of thermodynamic equilibrium, when *no solid solutions* occur in the solid–liquid system. However, when the system contains mixed crystals the approach of thermodynamic equilibrium between the entire solid and the liquid is seriously affected when the rate of mass transfer in the solid is limited.

Since mass transfer in the solid can hardly be promoted by external means and the diffusion constants in solids lie in the range of 10^{-10} to 10^{-12} cm^{-1} sec^{-1} (those of liquids are 10^{-4} to 10^{-5} cm^{-1} sec^{-1}), it even must be concluded that mass transfer within the solid is negligible under the experimental conditions usually applied in the determination of heating curves. Consequently only the surface layer of the solid participates in the thermodynamic equilibrium and the bulk of the solid is not in thermodynamic equilibrium during the determination of the melting curve.

These conclusions are used as the starting point for the interpretation of heating curves which is developed in this paper. On the basis of the new interpretation some discrepancies mentioned in the literature can be solved.

A further consequence of the lack of mass transfer in the solid is that the pretreatment of the sample influences the shape of the melting curve. This influence is absent when cooling curves are determined which start with the liquid sample.

However, since rates of crystallisation may be slow compared to rates of melting, serious deviations from the equilibrium temperatures may occur on cooling[1]. Therefore a heating curve obtained by starting with a solid sample is preferable.

Two cases of pretreatment of the sample may be distinguished:

1. The solid sample has been obtained by *slow freezing* of the liquid.
2. The solid sample has been obtained by *sudden freezing* of the liquid.

The present paper deals with gradually frozen samples. The heating curves of samples obtained by quick freezing will be discussed in another paper.

Relation between temperature and fraction liquid of a binary solid–liquid system which is slowly frozen

Since only the surface layer of the solid participates in the thermodynamic equilibrium, the amount of solid involved is negligible compared to the bulk of the solid. Since diffusion in the liquid is sufficiently large, the total amount of liquid present at a certain moment participates in the thermodynamic equilibrium.

Suppose that the total amount of liquid equals a fraction y of the total sample and let the concentration of the liquid be X_L (mol-fraction). The fraction of the sample which is solid is $(1 - y)$. Now suppose that the amount of solid increases with $d(1 - y)$. The concentration of this tiny deposit of solid is X_s which is coexistent with the liquid concentration X_L. Owing to the law of conservation of matter:

$$X_s \cdot d(1 - y) = -d\,(X_L\,y) \tag{1}$$

is valid, hence:

$$-\frac{dy}{y} = \frac{dX_L}{X_L - X_s} \tag{2}$$

According to thermodynamics (provided X_L and X_s are small)

$$(X_L - X_s) = \frac{Q}{RT^2}\,\Delta T \tag{3}$$

where

Q = heat of fusion in cal/mol.
R = gas constant in cal/degree mol.
T = temperature in °K
ΔT = depression of melting point in °C.

Further, if X_L is small, the following equation may be considered as a fair approximation:

$$X_L = K_L\,\Delta T \tag{4}$$

where K_L is a constant. Substitution of eqns. (3) and (4) in eqn. (2) yields:

$$-\frac{dy}{y} = \frac{K_L R T^2\, d(\Delta T)}{Q \cdot \Delta T}$$

Integration of the above equation results in:

$$-\ln y = \frac{RT^2}{Q} K_L \ln \Delta T + C \tag{5}$$

The concentration in the liquid X_L will be equal to X (the concentration in the total sample) when $y = 1$. Since, according to eqn. (4), $(\Delta T)_{y=1} = K_L/X$, the integration constant C will be equal to:

$$C = -\frac{RT^2}{Q} K_L \ln \frac{K_L}{X} \tag{6}$$

Combination of eqns. (5) and (6) results in:

$$\ln y = \frac{RT^2}{Q} K_L \ln \frac{X}{K_L \Delta T} \tag{7}$$

When no solid solutions are formed the constant K_L equals Q/RT^2 and eqn. (7) reduces to the simple and well-known equation of White obtaining to systems which show no miscibility in the solid phase:

$$y = \frac{RT^2}{Q} \frac{X}{\Delta T} \tag{8}$$

It may be useful to note that eqn. (7) is not restricted to solid–liquid systems. It is valid for any binary system showing a phase transition under the condition that the bulk of one of the phases is excluded from further exchange with the other phase. Since on heating of a slowly frozen sample the reverse process occurs, eqn. (7) is valid for the heating (melting) curve of a gradually frozen sample.

As was mentioned in the introduction, heating curves are preferred to cooling curves, because of the lack of *thermal* equilibrium on cooling. It is stressed that a limited lack of thermal equilibrium does not necessary imply perceptable deviations in the concentration of the coexisting phases. This view is fully confirmed by the experimental results mentioned below.

EXPERIMENTAL CHECK ON EQUATION (7)

An experimental check on eqn. (7) was carried out with two systems showing solid solutions, *viz.*: diphenyl (main component) – phenanthrene and tin (main component) – bismuth. Each component was carefully purified beforehand. Then the constant K_L of each system was determined independently of the heating curve:

Several mixtures of each system were prepared by weighing, followed by thorough mixing in the liquid phase. The mixtures were frozen and then their *final* melting point was determined as follows. The (macro) samples were slowly heated and a thermometer was inserted; heating was continued until a minute fraction of solid was present and then the sample was kept under adiabatic conditions and the temperature was read. At this moment the concentration of the liquid does not perceptably differ from the total concentration of the sample. This method yields results which are more reliable and reproducible than temperature readings taken at the moment the "last" crystal disappears (at that moment the contacting surface of solid and liquid is too small).

The final melting points thus found were plotted as a function of the concentration. The constant K_L of each system may then be read from the graph according to eqn. (4).

The heats of fusion (Q) of the main components were derived from the literature[4].

Subsequently, melting curves were determined on samples of known composition by means of the thin-film apparatus[5] operating according to the so-called dynamic method. The pretreatment of the sample consisted of melting the sample followed by gradual solidification within 30–60 min. The results obtained are presented in the first two columns of the Tables I, II and III. The third columns of these tables mention the depressions calculated with the aid of eqn. (7). Agreement between the temperatures observed and those calculated is striking. (The accuracy of the temperature readings is not better than 0.01°). For comparison, the depressions calculated on the basis of the equation which is valid in case of equilibrium between the liquid and the *total* mass of solid are listed in the fourth column of each table. This equation reads:

$$y = \frac{RT^2}{Q}\,\frac{X}{\Delta T} + \frac{K_s RT^2}{Q} \tag{9}$$

where K_s is the depression constant of the *initial* melting point. This constant was calculated from eqn. (3) and the already known value of K_L.

Clearly the difference between the depressions found and those calculated from eqn. (9) must increase when the fraction liquid (y) decreases. This is confirmed by the results.

TABLE I

DEPRESSIONS FOUND AND CALCULATED OF A SAMPLE OF DIPHENYL CONTAINING 0.181 mol% OF PHENANTHRENE

Fraction liquid y	Depression ΔT in °C Found	Calculated on the basis of local equilibrium. (eqn. 7)	Calculated on the basis of total equilibrium. (eqn. 9)
0.1	0.41	0.40	0.22
0.2	0.22	0.24	0.18
0.3	0.17	0.17	0.14
0.4	0.14	0.14	0.12
0.5	0.13	0.12	0.10
0.6	0.10	0.10	0.09
0.7	0.08	0.08	0.08

TABLE II

DEPRESSIONS FOUND AND CALCULATED OF A SAMPLE OF DIPHENYL CONTAINING 0.762 mol% OF PHENANTHRENE

Fraction liquid y	Depression ΔT in °C Found	Calculated on the basis of local equilibrium (eqn. 7)	Calculated on the basis of total equilibrium (eqn. 9)
0.1	1.85	1.86	0.95
0.2	1.03	1.02	0.77
0.3	0.77	0.77	0.64
0.4	0.62	0.61	0.55
0.5	0.54	0.53	0.49
0.6	0.47	0.48	0.43
0.7	0.42	0.43	0.39

TABLE III

DEPRESSIONS FOUND AND CALCULATED OF A SAMPLE OF TIN CONTAINING 0.300 mol% OF BISMUTH

Fraction liquid y	Depression ΔT in °C Found	Calculated on the basis of local equilibrium (eqn. 7)	Calculated on the basis of total equilibrium (eqn. 9)
0.1	2.82	2.90	1.84
0.2	1.82	1.83	1.40
0.3	1.42	1.41	1.22
0.4	1.18	1.15	1.08
0.5	1.02	1.00	0.98
0.6	0.92	0.92	0.90

DISCUSSION

The above results show that a formula derived on the assumption of local equilibrium (eqn. 7) fits the experimental melting curves more closely than a formula derived on the assumption of total equilibrium (eqn. 9). It may now be worthwhile to discuss the method by which the content of impurity in an unknown sample may be derived from the heating curve on the basis of the local equilibrium equation. Two methods of impurity determination are normally available, *viz.*: the so-called absolute and comparative methods. The absolute method demands only one heating curve. The data derived from the heating curve when combined with thermodynamic data (the depression constant and the distribution coefficient which are usually determined separately) may yield the amount of impurity. The comparative method demands two melting curves, one of the sample as such and one of the same sample after addition of a known amount of impurity.

Impurity determination by the absolute method

According to eqn. (7) a plot of ln y *versus* ln ΔT gives a straight line. The slope of this line gives the value of

$$-\frac{RT^2}{Q}K_L$$

and the line intersects the ln y-axis at

$$\ln y = \frac{RT^2}{Q}K_L \ln X/K_L$$

These data combined with the value of RT^2/Q (derived from the curve or from elsewhere) enable the value of K_L and X to be calculated by simple algebra. This procedure is possible provided that the melting point T_s of the pure main component is exactly known. When T_s is unknown, its value may be derived from the curve in the following way. Three values of y *viz.* y_1, y_2 and y_3 are chosen and the corresponding temperatures T_1, T_2 and T_3 are read from the curve. The pertaining values of ΔT are $T_s - T_1$, $T_s - T_2$ and $T_s - T_3$. From eqn. (7) it may be derived that:

$$\frac{\ln y_1/y_2}{\ln y_2/y_3} = \frac{\ln (T_s - T_2)/(T_s - T_1)}{\ln (T_s - T_3)/(T_s - T_2)} \tag{10}$$

The lefthand term of this equation is known; if its value is a then:

$$\left(\frac{T_s - T_3}{T_s - T_2}\right)^a = \frac{T_s - T_2}{T_s - T_1}, \quad \text{or}$$

$$(T_s - T_2)^{a+1} = (T_s - T_3)^a\,(T_s - T_1) \tag{11}$$

Now a series of plausible values of T_s is chosen and the values of the left and right terms of equation(11) are plotted as a function of T_s. The point of intersection of the two plots yields the desired value of T_s. This method of calculation, the determination of T_s included, has been applied to the data represented in the Tables I, II and III. The results are listed in Table IV. The results show that this method, although somewhat laborous, can give satisfactory results.

TABLE IV

COMPARISON OF THE AMOUNTS OF IMPURITY ADDED AND FOUND BY CALCULATION ACCORDING TO AN ABSOLUTE METHOD BASED ON EQUATION (7)

Substance	*Impurity added*	*Found*
Diphenyl	0.181 mol %	0.18 mol %
Diphenyl	0.762 mol %	0.74 mol %
Tin	0.300 mol %	0.28 mol %

Impurity determination by the comparative method

Eqn. (7), rewritten in its exponential form, reads:

$$y = \left(\frac{X}{K_L \Delta T}\right)^{\frac{RT^2}{Q} K_L} \quad , \quad \text{or}$$

$$(y)^{-\frac{Q}{RT^2 K_L}} = \frac{K_L}{X}(T_s - T)$$

In the following the temperatures obtaining to the heating curve of the sample are denoted by T_y, whereas those obtaining to the sample to which a known extra mol-fraction p of the impurity has been added, are denoted as T_y'. The difference of two temperatures obtaining to the first curve is:

$$T_{y_1} - T_{y_2} = \frac{X}{K_L}\left\{(y_1)^{\frac{-Q}{RT^2 K_L}} - (y_2)^{\frac{-Q}{RT^2 K_L}}\right\}$$

The difference of the corresponding temperatures of the second curve (read at the same values of y_1 and y_2) is:

$$T'_{y_2} - T'_{y_1} = \frac{X + p}{K_L}\left\{(y_1)^{\frac{-Q}{RT^2 K_L}} - (y_2)^{\frac{-Q}{RT^2 K_L}}\right\}$$

Thus:

$$\frac{T_{y_2} - T_{y_1}}{T'_{y_2} - T'_{y_1}} = \frac{X}{X + p} \qquad (12)$$

from which x may be solved. The above equation is identical with the equation previously derived by one of us[5] on the basis of the assumption of total equilibrium.

CONCLUSIONS

The equation obtaining to the comparative method of impurity determination, *viz.* eqn. (12), is applicable to a gradually frozen sample showing local equilibrium as well as to a sample showing total equilibrium. However, when the absolute method is applied, the equation valid for total equilibrium (eqn. 9) differs from eqn. (7) which is valid for total equilibrium of gradually frozen samples. These conclusions suggest a possible explanation of the discrepancy between authors who obtained satisfactory results on the impurity determination of solid solutions[5] and those who did not[6,7].

SUMMARY

A temperature-heat content relation is presented for binary systems which show solid solutions. Contrary to previous equations, the present equation accounts for the very restricted rate of diffusion in the solid. The equation is based on local equilibrium during freezing and melting. The equation obtaining to the comparative method of impurity determination and applicable to a gradually frozen sample is identical to the equation previously derived on the basis of total equilibrium. The corresponding equations of the absolute method differ considerably. Experiments confirm the local equilibrium theory and show the inadequacy of the total equilibrium theory.

RÉSUMÉ

Les auteurs ont effectué une étude sur la détermination des impuretés par analyse thermique, à l'aide de la courbe de fusion d'un échantillon refroidi lentement.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Bestimmung des Reinheitsgrades durch thermische Analyse der Substanzproben, die einer langsamen Abkühlung unterworfen waren.

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DETECTION AND COLORIMETRIC DETERMINATION OF POLYNITRO AROMATIC COMPOUNDS

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INTRODUCTION

Some new tests for polynitro compounds are investigated in this paper. As the literature on the utilization of polynitro organic compounds in organic analysis is so extremely extensive, any new analytical methods for these compounds should be capable of extensive modification and application.

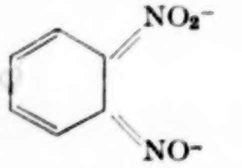
Benzene, which interferes with hematopoiesis, has been determined in the air by nitration to *m*-dinitrobenzene followed by reaction with alkaline butanone or acetone and measurement of the resultant violet color[1-3].

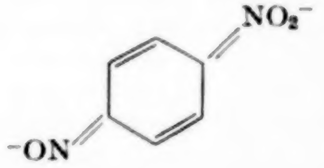
In a similar fashion, toluene, xylene, and chlorobenzene have also been determined by nitration to a *m*-dinitrobenzene derivative[4,5]. Recently a nitration test for polynuclear hydrocarbons was described in which pyrene, benzo[a]pyrene, chrysene, etc., could be detected in mixtures[6]. This test has been modified into a specific method for pyrene and its derivatives[7]. The latter procedure consisted of the preparation of polynitro pyrene derivatives which gave a blue color in alkaline solution. The method has been applied to the detection of pyrene in polluted air, auto exhaust fumes, and incinerator effluent.

Polynitro compounds have also been used as reagents in the analysis for creatinine[8] and 17-oxo steroids[9] in body fluids.

All these analytical procedures are examples of the general reaction of an aromatic compound containing two or three electron-attracting groups in meta positions with a suitably activated anion in alkaline solution to give a violet to purple quinonoidal anion[10]. Compounds such as *o*- and *p*-dinitrobenzene are reported to give colorless and yellow colors, respectively, in such a reaction[11,12].

However, *o*- and *p*-dinitrobenzenes are said to react with organic compounds which serve as hydrogen donors in an alkaline medium to give blue-violet and red quinonic dyes, respectively[13], *e.g.*





A third group of analytical methods is much more difficult to define as to mechanism. These methods include (a) the reaction of 1,2- and 1,4-dinitrobenzenes in alkaline solution with compounds containing the cyclopentadiene CH_2 group to give blue to green dyes[14] and (b) the reaction of 2,2′-dinitrobiphenyl and other polynitro compounds with dialkyl and aralkyl ketones to give violet and blue dyes[15]. The former reaction has been used to detect fluorene and the benzofluorenes in the air; the latter reaction has been used for the detection of dialkyl and aralkyl ketones.

In this paper these latter two reactions are applied to the detection or determination of polynitro aromatic compounds.

EXPERIMENTAL

Reagents

All compounds were obtained from the Fisher Chemical Co., Aldrich Chemical Co., and the K and K Laboratories or were prepared by standard literature procedures in the laboratory. Where necessary, chemicals were purified to a constant melting point.

Equipment

A Cary Model 11 Recording Spectrophotometer was used for wave length measurements. For time studies and preliminary investigations, an American Optical Company Rapid Scan Spectrophotometer was used.

Spot test procedure

To one drop (0.02 ml) of 25% aqueous tetraethylammonium hydroxide in a spot plate was added one drop of 5% fluorene (or 50% butanone) in dimethylformamide. Then one drop of the dimethylformamide test solution was added. The colors and identification limits are given in Tables I and II. For detection on paper the procedure was the same except that 1 µl of dimethylformamide test solution was added in the last step. In Table I the substitution of butanone for fluorene as a reagent gives almost identical results, except where noted in the table.

Colorimetric procedure

To 5 ml of the dimethylformamide test solution was added 5 ml of 0.1% fluorene in dimethylformamide, followed by 1 ml of 10% aqueous tetraethylammonium hydroxide and dilution to

TABLE I

COLORS AND IDENTIFICATION LIMITS FOR POLYNITRO COMPOUNDS DETECTED WITH THE FLUORENE TEST

Compound	*Color*[a]	*Ident. limit, µg*	
		Paper[b]	*Spot plate*
1,2-Dinitrobenzene	B	0.1	0.4
1,3-Dinitrobenzene	B[c]	0.1	0.2
1,4-Dinitrobenzene	G	0.1	0.2
1,2-Dinitro-4,5-dichlorobenzene	G[c]	0.1	0.5
2,3-Dinitro-N,N-dimethylaniline	G	0.5	2.5
2,4-Dinitrochlorobenzene	V[d]	0.05	0.2
2,4-Dinitrotoluene	B[d]	0.02	0.1
2,4-Dinitrophenylacetic acid	B[d]	0.01	0.2
2,4-Dinitroaniline	R[d]	0.01	0.2
3,5-Dinitrobenzoic acid	V[e,d]	0.1	0.2
3,5-Dinitrobenzoyl chloride	R[e,d]	0.05	0.1
Dinitromesitylene	G	2	2
Picryl chloride	R[d]	0.05	0.1
Picric acid	R[d]	0.05	0.1
2,4,6-Trinitroluene	R[d,f]	0.01	0.2
2,4′-Dinitrobiphenyl	B	0.5	1.
4,4′-Dinitrobiphenyl	YG	5.	10.
2,2′-Dinitrobiphenyl	B	0.5	1.
1,4-Dinitronaphthalene	G	0.05	0.5
1,6-Dinitropyrene	B	0.05	0.1
6,12-Dinitrochrysene	R	60.	0.5
1,3,6-Trinitropyrene	B[d]	0.05	0.2
1,3,6,8-Tetranitropyrene	B[d]	0.01	0.05

[a] B = blue; G = green; V = violet; R = red; Y = yellow.
[b] Colors not as stable on paper as on the spot plate.
[c] Purple in butanone procedure.
[d] Fluorene or butanone not necessary in the test.
[e] Blue in butanone procedure.
[f] Blue in fluorene test on paper.

TABLE II

COLORS AND IDENTIFICATION LIMITS FOR MISCELLANEOUS COMPOUNDS DETECTED WITH THE BUTANONE OR FLUORENE TESTS

Compound	*Butanone test*		*Fluorene test*	
	Color	*I.L., µg*	*Color*	*I.L., µg*
3-Nitroazobenzene	V	0.1	B	0.2
m-Bisphenylazobenzene	B	0.5	G[a]	0.1
3-Acetylazobenzene	R[b]	1	R[b]	2
β,3-Dinitrostyrene	R[a]	1	R[a]	2
4-Nitrobenzal-3-nitroaniline	R[c]	1	B[c]	0.5

[a] Blue in paper test.
[b] Yellow in paper test.
[c] Yellow-green in paper test.

50 ml with dimethylformamide. The absorption spectrum was then determined within 3 min. The wave length maxima and molar absorbances obtained with some polynitro compounds are shown in Table III. The results obtained in substituting other reagents for fluorene in the colorimetric determination of *o*-dinitrobenzene are presented in Table IV. In all cases the wave length maxima and the molar absorbance values were read directly after diluting the solution to the mark.

TABLE III

COLORIMETRIC DETERMINATION OF AROMATIC POLYNITRO COMPOUNDS WITH THE FLUORENE REAGENT

Compound	*Color*[a]	λ*max, m*μ	$\varepsilon \cdot 10^{-3}$
o-Dinitrobenzene	B	695	20.
p-Dinitrobenzene	G	705	16.
1,4-Dinitronaphthalene	G	738	13.
1,6-Dinitropyrene	G	655	13.
6,12-Dinitrochrysene	R	560	25.

[a] B = blue; G = green; R = red.

TABLE IV

EFFECT OF CHANGE OF REAGENT ON COLORIMETRIC DETERMINATION OF *o*-DINITROBENZENE

Reagent, 0.1% in DMF	*Color*[a]	λ_{max}*, m*μ	*Molar absorbance* $\varepsilon \cdot 10^{-3}$
Fluorene	B	695	20
2-Ethylfluorene	B	698	19
2-Bromofluorene	B	705	20
2-Fluorofluorene	B	700	18
2-Acetylfluorene	G	715	18
2-Benzoylaminofluorene	V	595	6.0
		660	6.0
Indene	B	660[b]	16
4H-Cyclopenta[d, e, f]phenanthrene	G	655	19
		700	20
11H-Benzo[b]fluorene	G	717	12

[a] B = blue; G = green; V = violet.
[b] Also shoulders at 600 and 700 mμ.

DISCUSSION OF SPOT TESTS

Unlike previously described color tests for polynitro compounds, *o*-, *m*-, and *p*-dinitrobenzene derivatives gave positive results, at least in the qualitative procedures. In other tests *m*-dinitro derivatives will usually give a color reaction while the *o*- and *p*-isomers will not, or vice versa, but the present test is considered a general test for most polynitro aromatic compounds. Not only that, but in the present method a brilliant, easily visible blue to green color was obtained for most tested dinitro aromatic compounds (Table I). Fluorene is used in this test, although butanone can be substituted with almost identical results. The few tested trinitro and tetranitro compounds gave the same color in alkaline dimethylformamide alone as was obtained with fluorene or butanone. With most of the other polynitro compounds, the presence of fluorene or butanone was necessary in the test procedure for the development of the color.

A few miscellaneous compounds were also tested and were found to give positive results even though in some cases a nitro group was not present. However, fairly strong electronegative groups were present (Table II). The positive results for these compounds can be explained, to some extent, as due to the general reaction of an aromatic compound containing two or three electron-attracting groups in the *meta* position with a suitably activated anion in alkaline solution to form a highly colored anion[10]. Consequently, compounds, such as 3-nitroazobenzene, 3-acetylazobenzene, 2-nitrofluorenone, etc., would be expected to give positive results.

The following compounds gave negative results in the spot test procedures: nitrobenzene, *p*-nitrophenol, *p*-nitroanisole, 4-nitro-1,2-xylene, 5-nitroacenaphthene, 1-nitropyrene 8-nitroquinoline, *p*-nitrocinnamic acid, 4,4′-dinitrobiphenyl, 1,5-dinitronaphthalene, and tetranitromethane.

DISCUSSION OF COLORIMETRIC PROCEDURE

Attempts to obtain quantitative results for *m*-dinitrobenzene by the colorimetric procedure were unsuccessful due to the rapid decolorization of the solution. The color obtained in the fluorene colorimetric procedure for *o*-dinitrobenzene gradually fades. A fresh solution has a molar absorbance of about 20,500. In 15 min the molar absorbance was 19,800; in 60 min the value had dropped to 19,300. For *p*-dinitrobenzene the color faded more rapidly (Fig. 1).

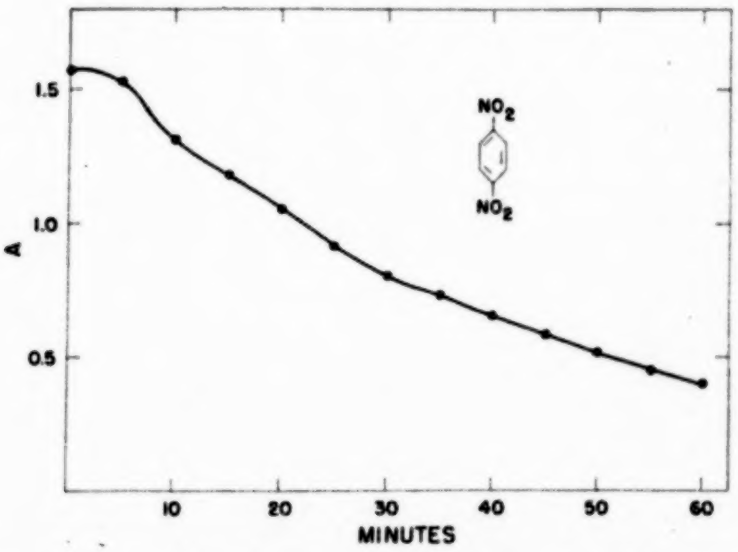


Fig. 1. Effect of time on the colorimetric determination of *p*-dinitrobenzene (10^{-4} *M*) with fluorene at λ_{max} 705 mμ by the standard procedure.

In the colorimetric determination of *o*-dinitrobenzene the use of higher or lower concentrations of the fluorene reagent decreased the color intensity. With the higher concentrations of fluorene ($\sim$10%), bands were also formed at 455, 485 and 520 mμ at the expense of the 695-mμ band.

Compounds containing strong electronegative groups other than the nitro groups could be expected to give the color reaction. For example, in the fluorene test, 3-nitroazobenzene gave a prominent band at 590 mμ, ε 20,000, with a shoulder at 700 mμ. Similarly, 1,3-bis-phenylazobenzene gave a dye with λ_{max} 665 mμ, ε 29,000. This latter value was obtained after 15–20 min standing as the color intensity takes that long to develop.

Other polynuclear hydrocarbons containing the cyclopentadiene moiety can be substituted for fluorene in the colorimetric procedure (Table IV). With 4H-cyclopenta[d, e, f]phenanthrene as reagent, a doublet was obtained in the absorption spectrum of the dye derived from reaction of the reagent with *o*-dinitrobenzene. With *m*-dinitrobenzene an unstable series of colors was observed, while with *p*-dinitrobenzene a prominent band was produced at 670 mμ with a shoulder at 700 mμ (Fig. 2).

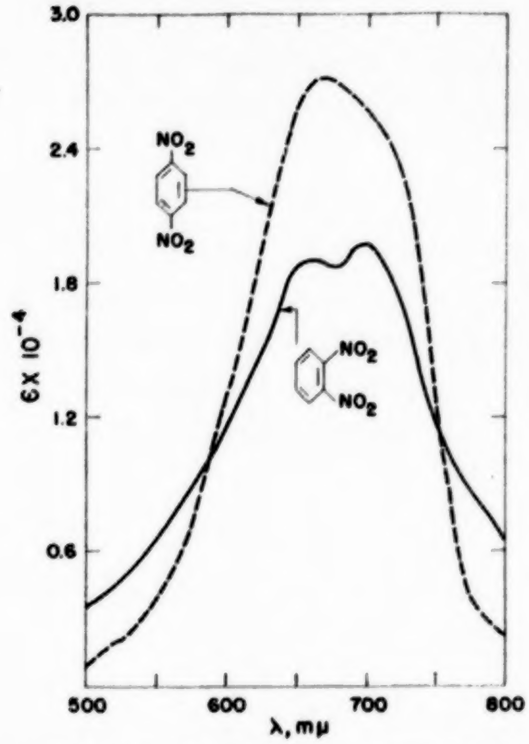


Fig. 2. Visible absorption spectra of the 4H-cyclopenta[d, e, f]phenanthrene procedure for the determination of *o*-dinitrobenzene (——) and *p*-dinitrobenzene (- - -). Both 10^{-4} *M*.

SUMMARY

A sensitive new spot test for polynitro aromatic compounds is introduced. In most cases a blue to green color is obtained using fluorene (or some other polynuclear cyclopentadiene derivative) as the reagent. A colorimetric procedure for the analysis of *o*- and *p*-dinitro compounds is also presented.

RÉSUMÉ

Une nouvelle réaction sensible est proposée pour l'identification des composés aromatiques polynitrés. On obtient avec le fluorène comme réactif une coloration bleue à verte. Une méthode de dosage colorimétrique est décrite.

ZUSAMMENFASSUNG

Aromatische Polynitroverbindungen geben mit Fluoren blaue bis grüne Färbungen. Diese Reaktion kann zum Nachweis wie auch zur colorimetrischen Bestimmung der aromatischen Polynitroverbindungen verwendet werden.

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SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM(III) WITH EDTA

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INTRODUCTION

Spectrophotometric determinations of chromium are generally based on the oxidizing action of chromium(VI) and require stringent conditions for accurate results. Very few methods are based on the complex-formation of chromium(III) in aqueous solution. This is probably due to the slow reactions of the strongly hydrated chromium(III) ions.

UBERBACHER AND DROSCHER[1] used the violet coloured chromium(III)-oxalate complex for the spectrophotometric determination of chromium.

An extremely stable complex of chromium(III) is formed with EDTA[2] but its formation is very slow at room temperature although it proceeds rapidly on heating. Several investigators have drawn attention to the possibility of a spectrophotometric determination of chromium by means of this complex[3-6]. In general their results are contradictory with respect to the dependence of the colour on pH, interferences by other ions, the excess of EDTA, etc. We therefore made a critical investigation of the conditions for the spectrophotometric determination of chromium(III) with EDTA.

As our results agree in many respects with those obtained by PŘIBIL AND KLUBALOVA[3], the publication of these authors can be taken as a starting point. PŘIBIL AND KLUBALOVA[3] found that the complex is readily formed in neutral or weakly acidic solutions simply by heating the solution containing chromium(III) and EDTA for 15 min. The purple coloured solution formed on heating turns blue on addition of alkali. When the pH rises above 11, complete decomposition of the complex takes place and $Cr(OH)_3$ precipitates.

EXPERIMENTAL PART

All chemicals used were of analytical grade. The content of the chromium(III) stock solutions was determined by the classical gravimetric procedure. A Unicam SP 500 spectrophotometer was used for all extinction measurements.

RESULTS

The chromium(III)–EDTA complex

Influence of the pH

We carried out a systematic investigation of the influence of the pH on the colour of the complex (ammonia–ammonium chloride and acetic acid–sodium acetate buffers were used). In acid solution two maxima occur, one at 395 mμ and another of larger intensity at 545 mμ. In alkaline medium the first maximum occurs at the same wavelength, but the extinction is considerably lower. The second maximum shifts to a higher wavelength, 590 mμ, and here the extinction is also lower. Table I gives the wavelength at which the second maximum occurs and the corresponding values of the molecular extinction coefficient.

TABLE I

DEPENDENCE OF THE SECOND MAXIMUM ON pH

pH	*Wavelength at which second maximum occurs*	*Corresponding molar extinction coefficient*
0.85	545	147
1.50	545	157
2.00	545	171
3.03	545	198
3.60	545	203
4.00	545	201
5.37	545	201
6.19	545	197
7.13	550	172
8.60	583	129
9.00	590	123
10.20	590	122
10.60	590	122
10.90	590	122

The second maximum proved to be most suitable for analytical purposes and accurate measurements showed that in two pH ranges the extinction is independent of the pH, *viz.*, at pH 3–6 and at pH 9–11.

Validity of Beer's law

We observed no deviation from Beer's law in either pH range. The molecular extinction coefficients of both maxima were calculated from 10 extinction measurements, being 201.2 (standard deviation 0.6) in acid medium (pH 3–6) at 545 mμ, and 122.1 (standard deviation 0.3) in alkaline medium (pH 9–11).

Interferences

In agreement with PŘIBIL AND KLUBALOVA[3] we found that:

(*a*) The extinction is independent of the excess of EDTA and of the time of heating. The colour is perfectly stable on standing.

(*b*) The following elements do not affect the formation of the complex and the resulting extinction: alkali metals; alkaline earth metals; elements of the H_2S group with the exception of copper; aluminium, manganese and zinc. Of the more common anions, chloride, nitrate, acetate and sulphate do not interfere (PŘIBIL *et al.*[3] mention an interference of sulphate ions, but we did not observe any interference even when the amount of sulphate was one hundred times that of chromium).

(*c*) Of the more common metals, only copper, iron, cobalt and nickel, which give coloured complexes with EDTA, interfere with the determination of chromium.

Determination of chromium as chromium(III)-EDTA complex in presence of other metals

Unfortunately, iron and nickel often occur in samples containing chromium. PŘIBIL *et al.*[3] therefore tried to develop a procedure for the separation of chromium(III) from these elements; potassium hydroxide and hydrogen peroxide were added to precipitate the interfering elements as their hydroxides and convert chromium to chromate. After filtration the chromate must be reduced to chromium(III) before the determination with EDTA. PŘIBIL stated that this reduction is incomplete with most common reducing agents. He used EDTA itself for the reduction of chromate to chromium(III). When potassium dichromate was used initially, the results of the determination as the EDTA complex were lower than expected from the results given directly by chromium(III), but they were reproducible and correct when used with an auxiliary calibration curve. However, when interfering elements were present and hydrogen peroxide had to be used for the separation, PŘIBIL found that it was impossible to remove the last traces of peroxide. According to PŘIBIL, the peroxide interferes with the chromium(III)-EDTA determination because it increases the extinction. This increase has an upper limit and he therefore added an excess of hydrogen peroxide to each determination. This resulted in a third calibration curve.

We reinvestigated these statements and at room temperature we could find no effect of hydrogen peroxide on the extinction at 545 mμ of an acid chromium(III)-EDTA solution, even when 100 ml of the solution of the complex contained 8 ml of 30% hydrogen peroxide. The extinction at 395 mμ increased but this was due to absorbance by hydrogen peroxide and was directly proportional to its amount. In alkaline medium and at higher temperatures the chromium(III)-EDTA complex was completely destroyed by hydrogen peroxide and chromium was converted to the hexavalent state.

We also proved spectrophotometrically that the reduction of dichromate by EDTA, as carried out by PŘIBIL, is not complete. In some, but not all, cases the spectrum of the reduced solution contained the characteristics of the spectrum of the dichromate ion. This fact could also be explained: as PŘIBIL mentions, not all the peroxide is decomposed by boiling; the residual amount could oxidize the residual dichromate in acid medium, to form blue chromium peroxide, CrO_5, or red perchromates. These colours were found in solutions that were oxidized with hydrogen peroxide to chromate and subsequently reduced to chromium(III) by means of EDTA.

Because of all these complications from oxidation to chromate and subsequent reduction, we concluded that a method which did not involve an oxidation, should be preferred. We succeeded in developing a few suitable procedures in which oxidation could be avoided before the determination as chromium(III)-EDTA. The three procedures given below cover practically all the cases likely to be met in practice.

Procedures A and B

The first two procedures (A and B) utilize the separation of chromium(III) by means of TAA (thioacetamide) and EDTA. (In previous papers[7-9] we have described the determinations of zinc, copper and iron by means of EDTA and TAA.)

We have shown[7], that addition of calcium chloride and TAA to an ammoniacal solution containing EDTA precipitates all the common group III elements, with the exception of chromium(III), provided that the solution is heated in a water bath before the addition of calcium chloride, because of the slow formation of the chromium(III)–EDTA complex at room temperature. It should therefore be possible to make use of this separation for the determination of chromium in presence of other group II and group III elements.

Procedure A can be used when cobalt and nickel are absent. The group II elements are precipitated if necessary (only when copper is present), in acid medium with TAA and the other interfering element (iron) as hydroxide, without the use of TAA, in ammoniacal medium. For the simple case when only group III elements are present, with the exception of cobalt and nickel, procedure A is as follows:

Place 2.5 ml of a solution, containing 0.15–4 mg of chromium(III) in a 15-ml centrifuge tube. If necessary, oxidize iron(II) to iron(III) with bromine water and heat to remove the excess of bromine. Add 1 ml of 0.2 *M* EDTA solution and heat for 30 min in a water bath at 90°. Cool and add ammonia until the colour of the solution changes from purple to blue. Add 1 ml of buffer pH 10, and 1 ml of 0.6 *M* calcium chloride solution and heat for another 30 min in a water bath at 95°. Cool, centrifuge and pour the supernatant liquid into a 25-, 50- or 100-ml volumetric flask, containing buffer solution of pH 10 or 4. Wash twice with 1 ml of a slightly ammoniacal 2% ammonium chloride solution into the flask, make up to the mark and measure the extinction at 590 or 545 mμ, depending on the buffer used.

The results of some of the determinations of small amounts of chromium in presence of 4 mg of iron are shown in Table II.

TABLE II

DETERMINATION OF DIFFERENT AMOUNTS OF CHROMIUM IN PRESENCE OF 4 mg OF IRON(III)

Wavelength of extinction measurement in mμ	*Cr(III)* present	*Cr(III)* found	*Error in %*
590	3.83 mg	3.84 mg	+0.25
545	0.765	0.776	+1.5
545	0.383	0.389	+1.5
545	0.383	0.387	+1.0
545	0.153	0.153	0
545	0.153	0.151	—1.3
545	0.153	0.152	—0.7

Very similar results were obtained when Al, Mn, and Zn were also added in the same amounts as iron. It may therefore be concluded that small amounts of chromium can be determined in this way in presence of relatively large amounts of Fe, Al, Mn and Zn.

Note

The same procedure can be used when group II elements are present, with the exception of copper. When copper is present it can be precipitated in acid solution with TAA before the precipitation of group III elements, or procedure B can be used.

Procedure B is used when cobalt or nickel is present; TAA is used to precipitate the interfering elements, Co, Ni and Cu. Of course procedure B could be followed in all cases, but procedure A is generally preferred, because the spectrophotometric determination can be carried out in acid solution (at 545 mμ). When the group III elements have been precipitated as sulfides with TAA, acidification of the filtrate results in turbidity which interferes with the extinction measurement, hence the extinction of the alkaline solution must be measured (at 590 mμ) when procedure B is applied. We have already shown[7], that group II and III elements, which interfere with this determination of chromium, can be precipitated by the addition of TAA and calcium chloride to the ammoniacal solution containing EDTA.

Procedure B is as follows. Place 2.5 ml of a solution, containing 0.7–4 mg of chromium(III) in a 15-ml centrifuge tube. Neutralize the solution with dilute ammonia (if a permanent precipitate appears, dissolve in a drop of hydrochloric acid). Add 3 ml of 0.2 *M* EDTA, heat for 30 min in a water bath at 90–95°, cool to 70°, add a few drops of ammonia (colour changes from purple to blue), 1 ml of buffer solution pH 10, 1.5 ml of an 8% solution of TAA and 200 mg of calcium chloride ($CaCl_2 \cdot 2\frac{1}{2}H_2O$). Heat for 30 min in a water bath at 80–85°. Centrifuge, remove the supernatant liquid by suction through a G4 glass filter stick. Wash twice with 2–3 ml water and combine the three filtrates in a 100-ml volumetric flask containing 20 ml of buffer solution pH 10. Make up to the mark and measure the extinction at 590 mμ.

Typical results obtained by this procedure, in presence of various elements, are given in Table III. It can be seen that only nickel interferes.

TABLE III

DETERMINATION OF CHROMIUM IN PRESENCE OF GROUP II AND GROUP III ELEMENTS

Other elements present, mg							*Cr(III), mg*		*Error in %*
Fe	*Al*	*Zn*	*Mn*	*Co*	*Cu*	*Ni*	*present*	*found*	
6	6	6	6	—	—	—	3.83	3.87	+ 1.0
3	3	3	3	3	3	—	3.83	3.88	+ 1.3
3	3	3	3	3	3	—	3.06	3.06	0
3	3	3	3	3	3	—	2.30	2.32	+ 0.9
3	3	3	3	3	3	—	1.54	1.57	+ 1.9
3	3	3	3	3	3	—	0.765	0.780	+ 1.9
—	—	—	—	—	—	3	3.83	4.42	+ 15

Notes

I. In the volumetric flask, the excess of TAA decomposes slowly, forming small amounts of hydrogen sulfide. It is therefore necessary to use absolutely cation-free distilled water, in order to avoid interference of traces of heavy metal sulfides.

II. The presence of nickel generally causes complications:

(*a*) Part of the nickel remains colloidal. This can be partly prevented by the addition of cobalt(II); nickel sulfide then coprecipitates with cobalt sulfide. Even then, however, the precipitation of nickel sulfide is usually only complete after several days.

(*b*) When precipitates of nickel sulfide come into contact with atmospheric oxygen, they can be oxidized so that some nickel dissolves[10] and causes in positive errors in the determination of chromium.

In spite of many efforts we were unsuccessful in developing a satisfactory quantitative separation of chromium(III) from nickel(II) which does not require a long time.

General remark with respect to procedures A and B

Larger amounts of the interfering elements than those mentioned in Tables II and III should be avoided, because decantations from centrifuge tubes with very large amounts of precipitate cannot be carried out satisfactorily.

Chromium(III) determinations in presence of larger amounts of these elements can be carried out by taking smaller amounts of the sample containing 0.2–1 mg of chromium.

Procedure C

Although procedures A and B gave correct results except in the presence of nickel, we tried to develop a procedure for the determination of chromium(III) in presence of nickel and perhaps other elements, which did not require a separation. We tried to utilize the following qualitatively observed facts.

(*a*) The chromium(III)–EDTA complex is formed very slowly at room temperature, whereas the complexes of the interfering elements are formed practically instantaneously.

(*b*) The complexes of the interfering elements absorb at 545 and 590 mμ, but to a much smaller extent than the chromium(III)–EDTA complex.

It should therefore be possible to determine chromium(III) in acid solution in presence of interfering metal ions by means of two extinction measurements at 545 mμ, one mixture with EDTA being heated and the other unheated. The difference of the two extinction measurements ΔE should then be equal to $\Delta \varepsilon c d$ in which $\Delta \varepsilon$ is the difference of the molecular extinction coefficients of the chromium(III)–EDTA complex and of chromium(III) itself.

The following results show that the requirements for this simple determination of chromium are fulfilled.

(*a*) *The velocity of the formation of the chromium(III)–EDTA complex.* We studied the increase in the extinction at 545 mμ with time in a 4-cm cell at room temperature of two 100-ml solutions containing about 10 mg of chromium, 5 ml of 0.2 *M* EDTA and buffered at pH 3.5 or 4 with acetic acid–acetate buffers. The increase of the extinction was linear with time during the first two hours. The extinction of the pure chromium(III) solution was 0.088 and that of the corresponding chromium(III)–EDTA solution after complex formation of the complex 1.52. The increase in the extinction at the beginning was 0.0005 per minute at pH 3.5 and 0.001 per minute at pH 4. These values prove that when a pH value of 3.5 is chosen and the extinction of the unheated solution is measured within 6 min the error in the determination caused by the formation of the EDTA complex is less than 0.2%.

(*b*) *Rate of formation of the interfering complexes, their molar extinction values and their behaviour on heating.* We found that the EDTA complexes of iron(III), nickel and copper were formed immediately after addition of EDTA to the metal ion solutions at pH 3.5 and 4. The extinction values were not affected by heating the solutions. The molar extinction values at the wavelength under consideration (545 mμ) were 4 for the iron(III)-complex, 5 for the nickel-complex and 3.5 for the copper-complex. Therefore no interference of iron(III), nickel and copper is to be expected in procedure C.

Although the cobalt(II)–EDTA complex is formed immediately at room temperature and the molar extinction coefficient is small, cobalt interferes because the extinction increases when the cobalt(II)–EDTA solution is heated, owing to the oxidation of the complex to Co(III)–EDTA, which is favoured by the decrease of the Co(III)/Co(II) oxidation potential in the presence of EDTA. Because the increase in the extinction of the cobalt(II)–EDTA solution on heating is small, interference with the determination of chromium(III) only occurs when cobalt is present in larger amounts than chromium.

Procedure C is as follows. It is applicable for chromium(III) solutions containing 0.1–1.5 mg of chromium per ml (about 10^{-2}–10^{-3} *M* Cr(III)) and various amounts of other metals.

Treat 5 ml of the solution in a test-tube with such an amount of 5% ammonia that the next drop of ammonia would cause precipitation of a metal hydroxide. Add 3 ml of 0.2 *M* EDTA (more when very large amounts of other metals are present). Heat the tube for 30 min in a water bath at 90–95°. Cool and transfer the liquid quantitatively to a 100-ml volumetric flask containing 10 ml of buffer pH 3.5 (prepared by diluting a mixture of 48 ml of acetic acid and 4.6 g of sodium acetate to 100 ml with water). Make up to the mark and measure the extinction in a 4-cm cell at 545 mμ. (For very small chromium concentrations, use a 50-ml flask, containing 5 ml of buffer solution.) Transfer another 5-ml aliquot of the original chromium(III) solution directly to another 100-ml volumetric flask containing 10 ml of buffer pH 3.5. Add water to a volume of 90–95 ml and then add 3 ml (more if necessary) of 0.2 *M* EDTA. Make up to the mark and measure the extinction immediately at 545 mμ in a 4-cm cell. The difference of the two extinction values $\Delta E = \Delta\varepsilon.c.d$, where $\Delta\varepsilon$ (the difference between the molar extinction coefficients of chromium(III)–EDTA and chromium(III)) is 189.6 and $d = 4$. The calculated c is simply related to the concentration of the original unknown solution.

Some of the results of determinations of chromium according to procedure C in presence of other elements are given in Table IV.

TABLE IV

DETERMINATIONS OF CHROMIUM IN PRESENCE OF OTHER METALS

Concentrations of other metal ions present (mmol)							*Concentration of chromium (mmol)*		*Error %*
Al	*Fe(III)*	*Zn*	*Mn*	*Co*	*Ni*	*Cu*	*present*	*found*	
—	20	—	—	—	20	20	8.86	8.92	+ 0.7
20	10	10	10	—	10	10	2.21	2.21	0
20	10	10	10	—	10	10	2.21	2.21	0
40	20	20	20	—	20	20	2.21	2.23	+ 0.9
40	20	20	20	—	20	20	2.21	2.24	+ 1.4
—	80	—	—	—	40	40	3.55	3.56	+ 0.3
—	80	—	—	—	40	40	3.55	3.59	+ 1.1
—	—	—	—	60	—	—	8.86	9.84	+11
—	—	—	—	20	—	—	8.86	9.22	+ 4
—	—	—	—	6	—	—	8.86	8.95	+ 1

The same procedure was applied to the determination of chromium in a N.B.S. chromium–nickel–steel (101 *d*), after dissolution of the alloy in concentrated hydrochloric acid. The alloy contained more than 70% Fe, about 0.2% Cu, 9% Ni, many traces of other elements and 18.67% Cr. We found with procedure C 18.70% and 18.73% Cr.

Notes

1. Any iron(II) must be oxidized to iron(III) with bromine water; the excess bromine is removed by boiling.

2. Contrary to procedures A and B, procedure C requires two aliquots of the same solution for the determination of chromium. 25 ml of the unknown solution, however, are sufficient (corresponding to at least 2.5 mg chromium).

3. As can be seen from Table IV accurate results for the determination of chromium can be obtained in presence of large amounts of the other elements under consideration, with the exception of cobalt. When the amount of cobalt present is smaller than the amount of chromium the error is negligible.

4. A great advantage of procedure C over A and B is that no separations are used. The time required for the determination of the chromium(III) content of a solution is less than an hour irrespective of the amounts and nature of the other elements under consideration (with the exception of cobalt).

SUMMARY

The spectrophotometric determination of chromium(III) as the chromium(III)-EDTA complex[3] has been critically investigated. The separation of chromium(III) from interfering elements by oxidation to chromate and subsequent reduction is unsatisfactory. Separation by means of TAA and EDTA is suggested; good results were obtained except in presence of nickel. A rapid method is also described for the determination of chromium(III); no separation is needed and results are accurate, except when more cobalt than chromium is present.

RÉSUMÉ

Le dosage spectrophotométrique du chrome(III), sous forme du complexe Cr(III)-EDTA, proposé par Přibil n'étant pas entièrement satisfaisant, deux autres procédés sont décrits, l'un avec séparation, sans oxydation du chrome(III); l'autre sans aucune séparation.

ZUSAMMENFASSUNG

Beschreibung von zwei spektrophotometrischen Methoden zur Bestimmung von Cr(III) als Cr(III)-EDTA Komplex. Bei der einen Methode werden die störenden Elemente als Hydroxyde und Sulfide gefällt, bei der anderen Methode ist keine Trennung notwendig.

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SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM(IV) WITH 1,1'-DIANTHRIMIDE

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INTRODUCTION

The organic reagent 1,1'-dianthrimide is normally used for spectrophotometric determination of small amounts of boron, the colour of the boron 1,1'-dianthrimide complex being developed in concentrated sulfuric acid by heating. During an investigation of the elements interfering in this determination it was found that germanium[1] and tellurium[2] also formed complexes with 1,1'-dianthrimide. Further investigations have shown that selenium reacts similarly, and in the present paper the use of 1,1'-dianthrimide for spectrophotometric determination of selenium is described.

No reference is made in the literature to the use of 1,1'-dianthrimide for the detection or determination of selenium.

INSTRUMENTS AND REAGENTS

Instruments

Extinction measurements were made with a Zeiss spectrophotometer PMQ II, a matched set of 0.500-cm glass cells being used.

Reagents

The sublimed selenium dioxide was of purum quality. 1,1'-Dianthrimide, concentrated sulfuric acid (95–97%), fuming sulfuric acid (about 20% SO_3) and other chemicals were of reagent grade quality. A series of sulfuric acids of varying strength was prepared by adding fuming acid or distilled water to concentrated sulfuric acid, the exact concentration being finally determined by titration. Ordinary distilled water from an all-metal still was used.

Glassware

All solutions were prepared and heated in 50-ml bottles (Jena Geräteglas) with ground-in glass stoppers.

Heat treatment

The solutions were heated in a thermostatically controlled drying oven of standard construction.

EXPERIMENTAL DATA

Standard solutions

Selenium dioxide (70.3 mg) was dissolved in about 25 ml of 1% sodium hydroxide solution. After dilution in a volumetric flask to 50 ml with 1% sodium hydroxide solution, the standard solution (containing 1 mg of selenium per ml) was stored in a plastic bottle. Another standard solution of selenium (containing 0.2 mg of selenium per ml) was prepared by diluting 10 ml to 50 ml with 1% sodium hydroxide solution. The 1% sodium hydroxide solution served as a blank.

1,1'-Dianthrimide (1.250 g) was dissolved in 96.12% sulfuric acid. The solution was diluted to 250 ml with the same acid and contained 5 mg of reagent per ml.

Absorption curves

In Fig. 1, curve 1, an absorption curve of the selenium 1,1'-dianthrimide complex is plotted. Curve 2 (Fig. 1) shows the absorption curve of a solution of 1,1'-dianthrimide.

The solutions measured photometrically were prepared in the following way. For curve 1, 0.6 ml of the selenium standard solution containing 0.2 mg of selenium per ml, 5 ml of the 1,1'-dianthrimide standard solution and 20 ml of 97.85% sulfuric acid were pipetted into a 50-ml bottle. The bottle was stoppered and the solution was mixed and then kept in the oven for 16 h at 70°. After cooling to room temperature the extinction at different wavelengths was measured against a blank consisting of 0.6 ml of 1% sodium hydroxide solution, 5 ml of 1,1'-dianthrimide standard solution and 20 ml of 97.85% sulfuric acid. The blank was also heated for 16 h at 70°. Curve 2 is the absorption curve of the blank solution measured against 96.12% sulfuric acid.

In this investigation the excess of 1,1'-dianthrimide was about 40 times the amount of selenium present. The high extinction values of the blank (as seen in Fig. 1, curve 2) can therefore be reduced considerably.

From Fig. 1 it is seen that the selenium 1,1'-dianthrimide complex has two absorption maxima at 480 and 585 mμ.

Effect of concentration of sulfuric acid

Before plotting calibration curves the effect of the concentration of sulfuric acid

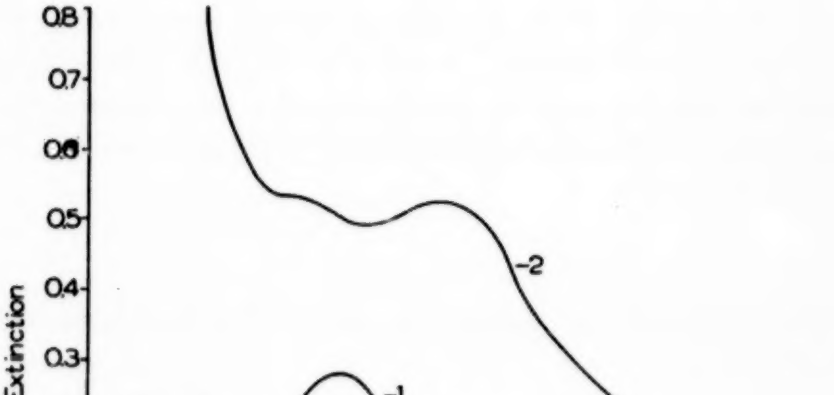

Fig. 1. Curve 1: Absorption curve of the selenium 1,1'-dianthrimide complex. Curve 2: Absorption curve of 1,1'-dianthrimide.

on the development of the colour of the complex was investigated for solutions heated for 16 h at 70°. A series of solutions was prepared in which the concentrations of selenium and 1,1'-dianthrimide were kept constant, while the concentration of sulfuric acid was varied.

0.1 ml of the selenium standard solution containing 1 mg of selenium per ml, 5 ml of 1,1'-dianthrimide standard solution and 20 ml of sulfuric acid of varying strength were pipetted into 50-ml bottles. The solutions were heated for 16 h at 70°, and the extinctions were measured at the wavelengths of the two absorption maxima against a series of blanks containing 0.1 ml of 1% sodium hydroxide solution, 5 ml of 1,1'-dianthrimide standard solution and 20 ml of the different acids. The extinction data obtained are given in Table I.

TABLE I

EFFECT OF CONCENTRATION OF SULFURIC ACID ON THE DEVELOPMENT OF THE COLOUR OF THE SELENIUM 1,1'-DIANTHRIMIDE COMPLEX

Concentration (%) of the 20 ml of sulfuric acid added:	*82.67*	*86.38*	*92.78*	*94.56*	*96.12*	*97.85*	*99.45*
Extinction at 480 mμ	0.285	0.362	0.386	0.338	0.324	0.364	0.578
Extinction at 585 mμ	0.445	0.501	0.525	0.469	0.418	0.432	0.610

It can be seen that the concentration of sulfuric acid is critical. In the present investigation 96.12% acid was employed for preparing the calibration curve.

Calibration curves

Calibration curves were plotted by measuring the extinctions of a series of solutions containing varying known amounts of selenium. Into a series of 50-ml bottles were pipetted known volumes up to 1 ml from the standard solutions of selenium. Volumes of less than 1 ml were diluted to that volume with the blank solution. Then 5 ml of 1,1'-dianthrimide standard solution and 20 ml of 96.12% sulfuric acid were added, and the solutions were heated for 16 h at 70°. The extinctions were finally measured at the wavelengths of the two absorption maxima against a blank prepared and heated in the same way. The calibration data are given in Table II; it can be seen that a positive deviation from the Beer-Lambert law was obtained within the concentration range examined.

TABLE II

EXTINCTION DATA FOR THE DETERMINATION OF SELENIUM WITH 1,1'-DIANTHRIMIDE

Se(mg) taken (C):	*0.02*	*0.06*	*0.10*	*0.14*	*0.18*	*0.20*	*0.25*
Extinction at 480 mμ(E_1)	0.026	0.123	0.308	0.500	0.710	0.850	1.222
Extinction index at 480 mμ(E_1/C)	1.30	2.05	3.08	3.57	3.99	4.25	4.89
Extinction at 585 mμ(E_2)	0.025	0.167	0.408	0.645	0.880	1.033	1.456
Extinction index at 585 mμ(E_2/C)	1.25	2.78	4.08	4.61	4.89	5.17	5.82

Effect of temperature and heating time

In concentrated sulphuric acid selenium and 1,1′-dianthrimide react very slowly. The rate of reaction increases with the temperature, but even at 70° the colour development is relatively slow. At temperatures above 70° a red colour appeared in addition to the colour of the complex; this colour probably originated from a decomposition product of 1,1′-dianthrimide. Consequently, a heating temperature above 70° cannot be recommended. A prolonged heating period also resulted in the appearance of the red decomposition product. A heating time of 16 h was used in this investigation.

Influence of foreign ions

On the basis of unpublished work on ions interfering in the determination of boron with 1,1′-dianthrimide, it can be deduced that the following ions interfere in the determination of selenium: B^{+3}, Ge^{+4}, Te^{+4}, Br^- (oxidized in concentrated sulfuric acid) and F^-. The interference from fluoride ions is probably due to attack on glass and release of boron.

The following ions were found not to interfere in amounts given in brackets in mg per 25 ml: Ag^+(2); Al^{+3}(5); Ba^{+2}(50); Bi^{+3}(1); Ca^{+2}(100); Cd^{+2}(50); Co^{+2}(20); Cr^{+3}(10); Cu^{+2}(20); Fe^{+2}(20); Li^+(10); Mg^{+2}(20); Mn^{+2}(10); Na^+(130); Ni^{+2}(20); Pb^{+2}(1); Si^{+4}(1); Sn^{+2}(20); Ti^{+4}(1); Tl^+(10); Zn^{+2}(50); Cl^-(200); $Cr_2O_7^{-2}$(0.01); PO_4^{-3}(100) and SO_4^{-2}(138).

Composition and stability constants of the 1,1′-dianthrimide complexes

The composition and the stability constant of the boron 1,1′-dianthrimide complex have been determined previously[3,4]. The complex was found to have the mole ratio 1 : 1, and the stability constant (in 93.8% sulfuric acid and at 70°) was found to be $1.4 \cdot 10^5$.

Investigations of the complexes of 1,1′-dianthrimide with germanium, tellurium and selenium showed that these complexes also have 1 : 1 mole ratios. Work on the stability constants, rates of formation etc. of these complexes is in progress and will be published later.

SUMMARY

In concentrated sulfuric acid selenium and 1,1′-dianthrimide form a complex with mole ratio 1 : 1 and with absorption maxima at 480 and 585 mμ. The complex formation can be utilized for spectrophotometric determination of up to about 0.2 mg of Se per 25 ml. Interfering ions are boron, germanium, tellurium, bromide and fluoride.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage du sélénium. On utilise comme réactif la dianthrimide-1,1′.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Selen mit Hilfe von 1,1′-Dianthrimid.

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ÉTUDE POLAROGRAPHIQUE DU GERMANIUM BIVALENT

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INTRODUCTION

Il existe relativement peu d'études polarographiques sur le germanium. La réduction du germanium(IV) a été signalée par plusieurs auteurs[1-4]; en milieu alcalin, la réduction se fait en un stade à l'état métallique et le courant limite de diffusion diminue progressivement au-dessus du pH = 8.5[4].

Réduit par l'acide hypophosphoreux, Ge(II) donne, en milieu acide, une vague anodique d'oxydation Ge(II) → Ge(IV), puis, à un potentiel plus négatif, une vague de réduction Ge(II) → Ge[5-7].

Il nous a paru intéressant de soumettre ce dernier système à une étude détaillée en vue d'obtenir des renseignements à la fois sur la chimie des solutions de germanium, encore très mal connues, et sur les phénomènes électrochimiques de cet élément. Cette publication comporte un certain nombre de résultats se rapportant à l'influence sur les deux vagues de germanium(II), de la concentration en acide hypophosphoreux et du pH.

DÉTAILS EXPÉRIMENTAUX

Tous les polarogrammes ont été obtenus, soit au moyen d'un appareil manuel, soit au moyen d'un appareil enregistreur Sargent dont l'échelle des potentiels est spécialement étalonnée. La transformation des courbes en log $(i_d - i)/i$ par exemple, en fonction du potentiel, a été effectuée en corrigeant les courants mesurés de la chute ohmique.

La réduction du germanium à la valence 2 est faite par l'acide hypophosphoreux H_3PO_2 (pK = 1.0); toutefois, comme Ge(II) s'oxyde instantanément à l'air, nous avons été obligés de réaliser un appareil permettant d'effectuer toutes les manipulations à l'abri de l'air: la réduction de la solution de Ge(IV) se fait à la température du bain-marie, sous atmosphère d'azote, la solution est amenée à un titre donné au moyen d'eau désoxygénée et enfin introduite dans une burette graduée. Les introductions dans la cellule polarographique se font également entièrement à l'abri de l'oxygène. Les précautions à prendre pour obtenir des résultats quantitatifs sont très sévères étant donné que les solutions sont toujours diluées en germanium et que, en plus, on a observé que l'introduction de traces d'oxygène provoque une oxydation *immédiate* de Ge(II) en Ge(IV).

La réduction totale d'une solution de germanium $5 \cdot 10^{-3}$ M par $H_3PO_2 \sim 1.7$ N à la température du bain-marie est obtenue après 2 h 30 de chauffage.

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* Cette étude fait partie de la thèse de doctorat: *,,Contribution au dosage et à l'étude polarographique du germanium''* (1958).

RÉSULTATS ET DISCUSSION

Comme nous l'avons déjà signalé, Ge(II), en milieu H_3PO_2, donne deux vagues de même hauteur: la vague anodique correspondant à l'oxydation Ge(II) → Ge(IV) est caractérisée par un potentiel $E^{1/2}$ égal à -0.149 ± 0.003 V/S.C.E., tandis que la vague cathodique — réduction Ge(II) → Ge — est située à -0.515 ± 0.002 V/S.C.E.; les constantes du courant de diffusion (DDC), pour une concentration en $[H_3PO_2] = 1.09$ N valant:

$$(\mathrm{DDC})_c = 3.36\ \mu\mathrm{A\ mg^{-2/3}\ sec^{1/2}}$$
$$(\mathrm{DDC})_a = 3.40\ \mu\mathrm{A\ mg^{-2/3}\ sec^{1/2}}$$

ces valeurs — potentiels $E^{1/2}$ et DDC — sont constantes pour des concentrations en germanium variant entre $5 \cdot 10^{-3}$ et $1.5 \cdot 10^{-4}$ ion g/l.

Nous allons examiner maintenant l'influence de la concentration en acide hypophosphoreux et du pH sur les vagues polarographiques ($E^{1/2}$, i_d, morphologie de la vague) en vue d'approfondir nos connaissances sur la chimie et l'électrochimie des solutions de germanium bivalent.

TABLEAU I

1ère série d'essais: $2.5 \cdot 10^{-3}$ M Ge + 0.008% gélatine
$(m^{2/3} \cdot \theta^{1/6})$ à -0.7 V/S.C.E. $= 1.83$; $(m^{2/3} \cdot \theta^{1/6})$ à -0.002 V/S.C.E. $= 1.82$ $\mathrm{mg^{2/3} \cdot sec^{-1/2}}$

$[H_3PO_2]$ N de la solution à polarographier	*$(i_d)_c$ μA*	*$(D.D.C)_c$ μA $mg^{-2/3}$ $sec^{1/2}$ $(mM)^{-1}$ × lit.*	*$(i_d)_a$ μA*	*$(D.D.C)_a$ μA $mg^{-2/3}$ $sec^{1/2}$ $(mM)^{-1}$ × lit.*
4.50	13.2	2.88	13.0	2.86
3.82	13.6	2.97	13.4	2.95
3.45	13.8	3.02	13.6	2.99
2.90	14.2	3.10	14.2	3.12
2.43	14.5	3.17	14.5	3.19
1.91	14.8	3.24	14.8	3.25
1.09	15.6	3.41	15.6	3.43
0.82	15.6	3.41	15.6	3.44

2ème série d'essais: $5 \cdot 10^{-4}$ M Ge + 0.008% gélatine
$(m^{2/3} \cdot \theta^{1/6})$ à -0.7 V/S.C.E. $= 1.81$; $(m \cdot \theta^{1/6})$ à -0.002 V/S.C.E. $= 1.805$ $\mathrm{mg^{2/3} \cdot sec^{-1/2}}$

$[H_3PO_2]$ N de la solution à polarographier	*$(i_d)_c$ μA*	*$(D.D.C)_c$ μA $mg^{-2/3}$ $sec^{1/2}$ $(mM)^{-1}$ × lit.*	*$(i_d)_a$ μA*	*$(D.D.C)_a$ μA $mg^{-2/3}$ $sec^{1/2}$ $(mM)^{-1}$ × lit.*
4.72	2.60	2.87	2.56	2.84
3.21	2.80	3.09	2.80	3.10
1.71	2.96	3.27	2.92	3.24
1.06	3.08	3.40	3.04	3.37
1.05	3.08	3.40	3.08	3.41
0.52	3.12	3.45	3.08	3.41
0.36	3.08	3.40	3.06	3.39
0.29	3.12	3.45	3.12	3.46
0.25	3.08	3.40	3.04	3.37

(*a*) *Influence de la concentration en H_3PO_2*

Pour une concentration constante en Ge(II), on observe une diminution progressive des hauteurs dex deux vagues lorsque la concentration en H_3PO_2 augmente (voir Tableau I).

Cette diminution de $(id)_a$ et $(id)_c$ peut être due soit à l'augmentation de la viscosité du milieu, soit à une modification de la dimension de la particule diffusante. D'après la relation de Stokes-Einstein, on sait que le coefficient de diffusion D doit être inversement proportionnel à la viscosité η du milieu et, comme le courant limite i_d est proportionnel à $D^{1/2}$ (équation d'Ilkovic), on peut s'attendre à ce que $i_d\,\eta^{1/2}$ soit une constante s'il s'agit d'un effet de viscosité. Les mesures ont été faites au viscomètre d'Oswald à 25° ± 0.5 par rapport à l'eau distillée ($\varrho_0 = 0.9919$ g/cm³, $t_0 = 209$ sec):

$$\frac{\eta_s}{\eta_0} = \frac{\varrho_s}{\varrho_0} \cdot \frac{t_s}{t_0}$$

Le Tableau II montre que le produit de i_d par $\eta^{1/2}$ est bien constant à moins de 1% près, ce qui constitue la précision de la mesure des courants en polarographie ordinaire.

TABLEAU II

Série de mesures no. 1: ○ (rapporté à une concentration $5 \cdot 10^{-4}$ *M* en Ge)
Série de mesures no. 2: △ ($5 \cdot 10^{-4}$ *M* en Ge)

Série	$[H_3PO_2]$ *en N*	$(i_d)_c$ *en µA*	t_s *min*	ϱ_s g/cm³	η_s/η_0	$i_d[\eta_s/\eta_0]^{\frac{1}{2}}$
△	4.72	2.60	5'15"	1.109	1.685	3.38
○	4.50	2.64	5'12"	1.106	1.660	3.39
○	3.82	2.72	4'53"	1.089	1.540	3.37
△	3.21	2.80	$4'40''\frac{6}{10}$	1.076	1.456	3.38
△	1.71	2.96	4'12"	1.039	1.255	3.32
△	1.06	3.08	$3'54''\frac{6}{10}$	1.024	1.160	3.32
○	1.06	3.10	3'55"	1.024	1.162	3.35
						moyenne = 3.36 ± 0.02

L'influence de la concentration en H_3PO_2 sur les potentiels de demi-vague et sur la forme de la courbe est de nature à nous fournir des indications précieuses. Les résultats expérimentaux sont groupés dans le Tableau III.

Tableau III contient non seulement les potentiels de demi-vague des vagues anodiques et cathodiques mais également les pentes des droites θ_a et θ_c obtenues en représentant les vagues en fonction de

$$\log \frac{(i_d)_c - i}{i} \text{ et } \log \frac{-i}{i - (i_d)_a};$$

les pentes permettent alors de calculer $(n\,\alpha)_c$ et $(n\,\beta)_a$, α et β étant les coéfficients d'activation et n le nombre d'électrons intervenant dans la réaction lente, ainsi qu'il résulte de l'équation théorique d'une vague irréversible.

De l'ensemble de ces résultats, il résulte que:

(*1*) la vague cathodique correspond à la réduction du germanium(II) à l'état métallique, en formant vraisemblablement un amalgame: elle est du type réversible ($\alpha = 1$) et donne un nombre d'électrons $n = 2$.

(*2*) le déplacement du potentiel $(E^{1/2})_c$ avec l'augmentation de la concentration en acide hypophosphoreux vers des potentiels plus négatifs semble indiquer l'existence d'un complexe hypophosphoreux de Ge(II).

(*3*) la vague anodique possédant un D.D.C. sensiblement égal à celui de la vague

TABLEAU III

Sol: $5 \cdot 10^{-4}$ *M* Ge + 0.008% gélatine
Série ⊙ : essais – mai 1957
Série ⊡ : essais – janvier 1957
Séries △ et × : essais – mai – juin 1956.

Série	$[H_3PO_2]$ *N*	$\log[H_3PO_2]$	$E^{\frac{1}{2}}_{a}$ *V/S.C.E.*$_c$	$E^{\frac{1}{2}}_{e}$ *V/S.C.E.*	*R* *Ohms*	θ_c *mV*	θ_a *mV*	$(n\alpha)_c$	$(n\alpha)_a$
⊙	4.72	+0.674	—0.539	—0.142	600	31.2	58.7	1.90	1.00
⊙	3.21	+0.506	—0.531	—0.143	550	31.7	60.0	1.86	0.99
⊙	1.71	+0.232	—0.524	—0.146	850	30.5	61.2	1.94	0.97
⊙	1.06	+0.027	—0.512	—0.152	900	30.0	61.5	1.97	0.96
⊙	1.05	+0.024	—0.513	—0.150	950	30.0	63.2	1.97	0.93
×	0.94	—0.028	—0.512	—0.176	900	30.0	56.2	1.97	1.05
⊡	0.76	—0.117	—0.509	—0.158	—	—	—	—	—
×	0.75	—0.125	—0.505	—0.157	950	30.0	58.7	1.97	1.00
⊡	0.72	—0.143	—0.505	—	—	—	—	—	—
△	0.64	—0.194	—0.501	—	—	—	—	—	—
⊡	0.58	—0.233	—0.503	—0.157	—	—	—	—	—
×	0.54	—0.269	—0.498	—0.176	1650	30.0	61.5	1.97	0.98
⊙	0.52	—0.286	—0.500	—0.156	1250	32.4	63.7	1.83	0.93
△	0.50	—0.298	—0.497	—	—	—	—	—	—
⊡	0.49	—0.308	—0.498	—0.157	—	—	—	—	—
△	0.42	—0.377	—0.494	—	—	—	—	—	—
⊙	0.37	—0.437	—0.492	—0.160	1450	30.0	62.5	1.97	0.95
⊙	0.29	—0.542	—0.485	—0.169	1900	30.0	60.0	1.97	0.90
⊙	0.25	—0.605	—0.482	—0.171	1400	—	—	—	—
×	0.21	—0.684	—0.480	—	1650	30	58.7	1.97	1.00

Les indications *c* et *a* se rapportent respectivement à la vague cathodique et anodique.

cathodique, correspond par conséquent à l'oxydation Ge(II) — Ge(IV). La valeur de $n\beta$ indique indubitablement le caractère irréversible de cette réaction d'électrode et le léger déplacement de $(E^{1/2})_a$ en fonction de la concentration en acide hypophosphoreux semble confirmer le fait que Ge(II) est complexé par l'acide en question.

Si l'on examine maintenant les déplacements de $E^{1/2}$ en fonction de la concentration en acide hypophosphoreux, on trouve, pour la vague cathodique, une variation linéaire aussi bien en portant $(E^{1/2})_c$ en fonction de log $[H_3PO_3]$ que en fonction de log $[H_2PO_2]^-$; les pentes de ces droites permettent de déterminer la valeur du nombre de particules dans le complexe (puisque $n = 2$) et l'on trouve, dans le 1er cas, n = 1.83 et dans le second 3.3.

Il est impossible, sur la base de ces données, de trancher entre les complexes $Ge(H_3PO_2)_2^{+2}$ ou $Ge(H_2PO_2)_3^-$.

Les cas de la vague anodique est trop complexe et la discussion des résultats ne mène à aucune hypothèse ayant quelque valeur.

(*b*) *Influence du pH*

L'influence du pH est représentée dans la Fig. 1. Il n'est pas possible de faire une discussion détaillée de ces résultats dans le cadre de cet article. Nous voudrions simplement indiquer les conclusions essentielles qui en résultent:

Notons d'abord que la diminution de i_d observée à pH > 1.0 représente un état d'équilibre réversible et qu'il ne s'agit pas du résultat d'une précipitation d'hydroxyde; on observe d'ailleurs simultanément un déplacement de $E^{1/2}$ dans le sens des potentiels négatifs pour les deux vagues; des mesures turbidimétriques n'ont laissé apparaître aucune indication de formation de solution colloïdale. Il semble plutôt s'agir d'une transformation progressive du complexe par exemple $Ge(H_3PO_2)_2^{+2} \rightarrow Ge(H_2PO_2)_2$, au fur et à mesure de l'augmentation du pH, nouvelle forme irréductible ou en tous cas avec une vitesse très faible.

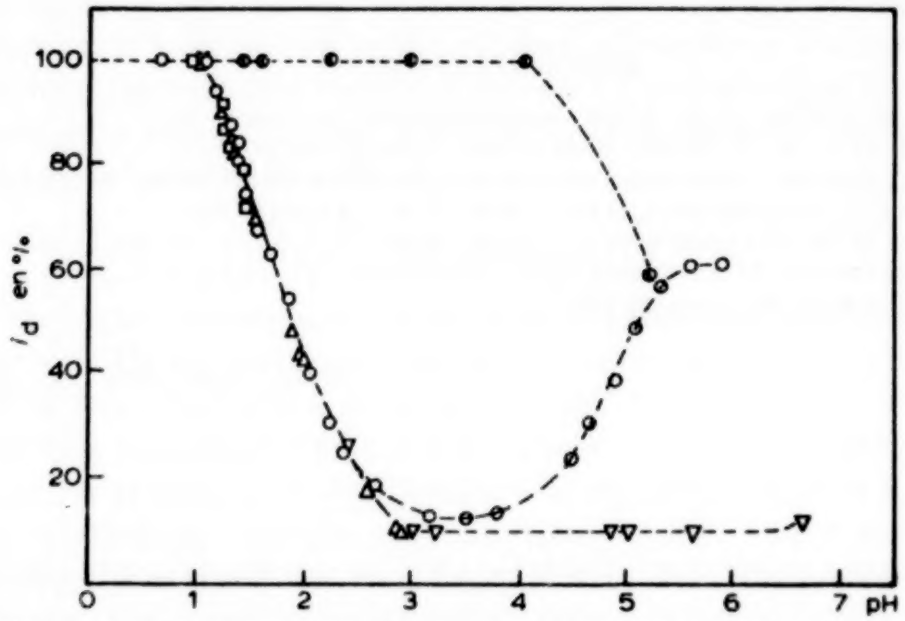

Fig. 1. Variation de i_d en % en fonction du pH, (sol. $5 \cdot 10^{-4}$ *M* Ge(II) + 0.25 *M* H_3PO_2 + 0.008% gélatine). ○ : avec NaAc seul (mesures 1957); □ : avec NaAc seul (mesures 1956); △ : avec NaOH seul; ▽ : avec biphtalate de K + NaOH; ◐: avec $K_2C_2O_4$ 0.05 *M* + KOH.

L'augmentation de la vague, en milieu acétique à pH > 4, semble indiquer la transformation du complexe hypophosphoreux en complexe acétique.

Enfin, l'étude en milieu hypophosphoreux et oxalique à différentes concentrations et différents pH — étude portant sur le courant limite et sur la forme de la vague — tend à montrer que l'on assiste progressivement, avec l'accroissement du pH au delà de 1, à la formation de complexe oxalique, $Ge(C_2O_4)$ s'oxydant en $Ge(C_2O_4)_3^{-2}$ vers pH = 3. La diminution ultérieure à pH > 4 doit être attribuée à la formation d'un sel basique insoluble.

RÉSUMÉ

Les auteurs ont fait une étude polarographique des vagues de réduction et d'oxydation de Ge(II) dans différents milieux — notamment acide hypophosphoreux et acide oxalique — en fonction du pH et de la concentration. La vague de réduction de Ge(II) dans H_3PO_2 1.09 *N* est caractérisée par $E^{1/2} = -0.515 \pm 0.002$ V/S.C.E. et une constante du courant de diffusion de 3.36 μA mg$^{-2/3}$ sec$^{1/2}$ tandis que pour la vague d'oxydation, on trouve $E^{1/2} = -0.149 \pm 0.03$ V/S.C.E. et D.D.C. = 3.40 μA mg$^{-2/3}$ sec$^{1/2}$. Cette étude fournit des indications sur les complexes formés.

SUMMARY

The authors made a polarographic study of the oxidation and reduction waves of Ge(II) in different media — hypophosphorous acid and oxalic acid in particular — in relation to pH and

concentration. In 1.09 N H_3PO_2 the reduction wave of Ge(II) is characterized by $E^{1/2} = -0.515 \pm 0.002$ V/S.C.E. and a diffusion current constant of 3.36 μA mg$^{-2/3}$ sec$^{1/2}$, whereas for the oxidation wave these values are $E^{1/2} = -0.149 \pm 0.003$ V/S.C.E. and D.D.C. = 3.40 μA mg$^{-2/3}$ sec$^{1/2}$. This study gives some information about the complexes that are formed.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss von pH und Konzentration auf den Verlauf der Oxydations- und Reduktionskurven bei der polarographischen Bestimmung von Ge(II) in verschiedenen Medien.

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THE POLAROGRAPHIC DETERMINATION OF THIOETHANOLAMINE AND ITS DISULFIDE IN THE PRESENCE OF ONE ANOTHER

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Thioethanolamine and its disulfide have been found to afford protection against ionizing radiation for a number of biological systems[1-4]. In order to elucidate the mechanism of protection of these compounds, it is necessary to determine thioethanolamine in the presence of its disulfide at the physiological pH value of 7.4.

Most methods for the determination of the disulfide group involve prior reduction with subsequent determination of the mercaptan formed. IIJIMA AND EGUCHI[5] have reported a method for disulfide based on the color produced after reaction of the disulfide group with copper sulfate and sodium thiosulfate. BENESCH AND BENESCH[6] proposed an indirect titration procedure involving back titration of the excess of added iodoacetamide. The anodic polarography of sulfur compounds in petroleum and its fractions has been reported by DRUSHEL AND MILLER[7].

The procedure described in the present paper is a direct polarographic method involving the mercury dissolution wave.

REAGENTS AND APPARATUS

Thioethanolamine as the hydrochloride was obtained from Evans Chemetics, Inc., New York City. The disulfide of thioethanolamine (β, β'-diaminoethyl disulfide dihydrochloride) was obtained from K & K Laboratories, Inc., Jamaica, New York.

All other reagents were of "analytical grade". Polarograms were run in a CLARK and LUBS buffer of pH 7.4, ionic strength 0.2 M.

A Leeds and Northrup Electro-Chemograph, Type E, was used throughout. The dropping mercury electrode had a capillary constant ($m^{2/3}t^{1/6}$) of 2.211 mg$^{2/3}$ sec$^{-1/2}$. A Lingane H-cell fitted with a potassium chloride-agar plug and a saturated calomel electrode was used as the polarographic cell. This cell was placed in a water bath thermostated at 25 ± 0.2°. Nitrogen gas was bubbled through the test solutions for fifteen minutes prior to each run and a nitrogen atmosphere was maintained above the solution during the course of the run. Commercial tank nitrogen (Southern Oxygen Co.) was purified by passing the gas through two solutions of chromous sulfate and one of buffer before entering the H-cell.

DISCUSSION OF RESULTS

In Fig. 1 are shown the polarograms of thioethanolamine and its disulfide in a buffer medium of pH 7.4. Thioethanolamine has a half-wave potential of —0.420 V *vs.* SCE and its disulfide has a half-wave potential 200 mV more negative. The wave of the disulfide exhibits a maximum which can be suppressed by the addition of two drops of a 0.2% solution of gelatin. Thioethanolamine was found to give a linear current-concentration relationship over the concentration range of $2 \cdot 10^{-5}$ to 10^{-2} molar and the disulfide over the range of $7.5 \cdot 10^{-6}$ to $7.5 \cdot 10^{-3}$ molar. These substances could be determined singly with an average error of less than 2%. In admixture, the disulfide could be determined in the presence of a 100-fold excess of thioethanolamine and the

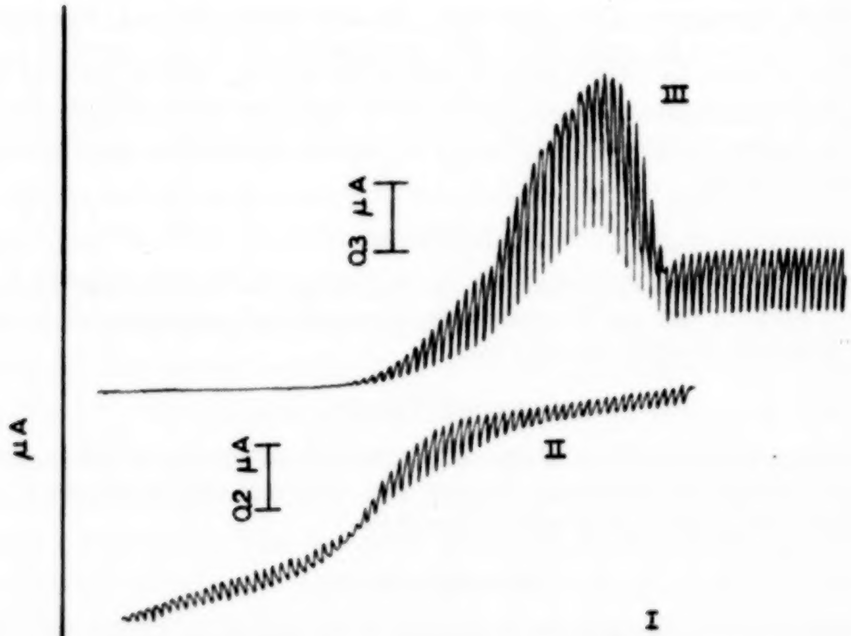

Fig. 1. Polarograms of thioethanolamine and its disulfide in a buffer solution of pH 7.4. Curve I. Supporting electrolyte alone. Curve II. 10^{-4} M thioethanolamine. Curve III. 7.5 (10^{-4}) M disulfide of thioethanolamine.

mercaptan in the presence of a 10-fold excess of the disulfide with an average error of less than 5%.

Effect of air

In the buffer medium in which this determination is performed, thioethanolamine is rapidly air oxidized to the disulfide. A polarogram run on thioethanolamine showed no disulfide to be present. After exposure of the test solution to the air for 30 min, the wave for the mercaptan had completely disappeared and was replaced by the wave for the disulfide.

This sensitivity to air oxidation makes it necessary to deaerate both the thioethanolamine and the buffer solution prior to mixing and to add the test solution to the buffer in a manner which excludes all but traces of air. This can be accomplished by placing the buffer solution in the polarographic cell, flushing with nitrogen gas, and adding the thioethanolamine solution from a pipette, the tip of which is below the surface of the buffer solution.

ACKNOWLEDGEMENT

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SUMMARY

A direct polarographic method has been developed for the determination of thioethanolamine and its disulfide in the presence of one another. Thioethanolamine may be determined over the concentration range of $2 \cdot 10^{-5}$ to 10^{-2} molar and its disulfide over the range of $7.5 \cdot 10^{-6}$ to $7.5 \cdot 10^{-3}$ molar with an average error of 2%. Thioethanolamine may be determined in the presence of a 10-fold excess of the disulfide and the disulfide in the presence of a 100-fold excess of the mercaptan. Precautions must be taken to exclude air from the system due to the rapid oxidation of the thioethanolamine to its disulfide.

RÉSUMÉ

Une méthode polarographique est proposée pour le dosage de la thioéthanolamine et de son disulfure, en présence l'un de l'autre. En raison de la rapidité d'oxydation de la thioéthanolamine, il est nécessaire d'éliminer complètement l'air.

ZUSAMMENFASSUNG

Beschreibung einer polarographischen Methode zur Bestimmung von β-Mercaptoäthylamin neben der entsprechenden Disulfidverbindung. Wegen der leichten Oxydierbarkeit der Mercaptoverbindung muss unter Luftausschluss gearbeitet werden.

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MACRO- ET MICRODOSAGE DE TRACES DE COBALT

DOSAGES SPECTROPHOTOMÉTRIQUE ET POLAROGRAPHIQUE DU COBALT DANS LES ACIERS MA 2 B, EDELWEISS

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DOSAGE SPECTROPHOTOMÉTRIQUE

Il est nécessaire de connaître la teneur en cobalt des matériaux utilisés dans la construction des réacteurs atomiques et susceptibles de recevoir un flux intense et prolongé de neutrons. En effet, il faut éviter, dans la mesure du possible, la formation de trop grandes quantités de cobalt 60, isotope de longue période, émetteur de rayons γ pénétrants.

Parmi les divers procédés de séparations proposés pour le dosage du cobalt dans les aciers, citons celui de SMOCZKIEWICZOWA ET MIZGALSKI[1] qui utilisent la chromatographie sur papier et de SAYLER ET AWEET[2] qui effectuent une séparation électrolytique sur anode. Dans ce dernier cas, les quantités d'échantillons nécessaires sont relativement très grandes puisque la solution doit renfermer 10 mg environ de cobalt; il ne semble donc pas qu'elle puisse s'appliquer au dosage d'aciers très pauvres en cobalt. D'autres auteurs déposent le cobalt sur une cathode de mercure, puis dissolvent celle-ci dans une atmosphère d'azote. Il est aussi proposé une extraction à l'α-nitroso-β-naphthol[3,4]. PEPKOWITZ ET MARLEY[5] ont mis au point une méthode rapide et précise de dosage du cobalt par le tétraphénylarsonium mais elle n'est pas suffisamment sensible, semble-t-il, pour le dosage de faibles traces de cobalt dans les alliages. Citons encore GRAUE *et al.*[6] dont la méthode a été spécialement établie pour les alliages destinés à la construction des réacteurs. Ils partent de 1 g d'échantillon; le fer est éliminé par extraction à l'éther chlorhydrique ou par entraînement à l'oxyde de zinc.

Pour le dosage, la plupart des auteurs utilisent la méthode spectrophotométrique et comme réactif le nitroso-sel R, particulièrement sensible. Nous proposons une détermination du cobalt dans l'acier 18/8 par ce même réactif, le mode opératoire est basé sur l'étude systématique que nous avons faite sur cet élément tant en ce qui concerne les séparations que la détermination spectrophotométrique. La précision et la sensibilité de la méthode ont été déterminées, les pertes et contaminations ont été évaluées[7-9].

Cette méthode est plus sensible que celles proposées dans la littérature, grâce à un mode opératoire différent, à l'emploi de microcuves et d'un photomultiplicateur. On peut doser des traces de cobalt comprises entre 0.01 μg et 50 μg dans les milieux les plus complexes, tant chimiques que biologiques, avec précision et sans difficultés spéciales.

Bien que la plupart du temps, une telle sensibilité ne présente pas une absolue nécessité, même pour des matériaux destinés à l'énergie atomique, elle a néanmoins le très grand avantage de permettre d'opérer sur de très faibles quantités d'échantillon. On diminue le temps nécessaire aux diverses opérations, certaines d'entre elles peuvent même être supprimées et on évite du même coup la présence de trop grandes quantités d'ions étrangers, le fer dans le cas particulier. On peut objecter qu'en diminuant la prise dans de telles proportions, la moindre perte ou la plus faible contamination sont susceptibles de provoquer de grandes erreurs. Cet argument est sans valeur car les réactifs utilisés sont purifiés de telle sorte que le blanc est très souvent négligeable et de toute façon, il peut être déterminé très exactement. De plus, en réduisant la quantité d'échantillon, on réduit du même coup la quantité des réactifs nécessaires et par conséquent les contaminations. Quant aux pertes, nous verrons qu'elles diminuent avec la prise et qu'elles ne sont pas plus fortes, proportionnellement sur 100 mg que sur 1 mg d'échantillon (v. Tableaux I et II). Il est du reste possible de les évaluer avec précision par addition, à la solution initiale, d'un indicateur radiochimique, en l'occurrence le cobalt 60, dont l'activité γ est mesurée, au compteur à scintillation, au début puis à la fin des opérations analytiques. La perte d'activité correspond de façon très exacte aux pertes de cobalt au cours de l'analyse.

Cet indicateur radiochimique permet aussi de contrôler l'efficacité des séparations et de suivre pas à pas la marche de l'analyse. Cette manière de faire a considérablement facilité la mise au point de la méthode. Evidemment, nous sommes placés dans des conditions particulièrement avantageuses car notre indicateur a une longue période et les rayons γ qu'il émet, très pénétrants, sont particulièrement faciles à compter avec précision. De plus, le processus présente une grande sensibilité.

Les densités optiques ont été mesurées au spectrophotomètre "Beckman DU avec ou sans photomultiplicateur et les mesures d'activité γ au moyen d'un scintillateur P 20 B équipé d'un cristal creux et relié à un compteur "Tracerlab 1000 scaler". Pour le marquage des solutions, nous avons utilisé le cobalt 60 (solution ayant une activité de 1 μc/ml et renfermant 0.18 μg/ml de cobalt total).

Pureté des réactifs

Nous avons utilisé des acides "Merck pro anal."; le cobalt s'y trouve en quantité négligeable. Quant au citrate de sodium, régulateur de pH et agent complexant, il contient au maximum 0.5 μg de cobalt par 100 g. Toutes les solutions ont été préparées avec de l'eau bidistillée préalablement traitée aux échangeurs de cations. Un blanc permet de faire les corrections des erreurs provenant des contaminations.

MACRODOSAGE

Mode opératoire

On dissout 100 à 500 mg d'acier dans 15 ml d'eau régale (l'analyse sur 1 g, proposé par certains auteurs n'est pas à recommander ici). On porte à ébullition pour éliminer le chlore et on ajoute de temps en temps un peu d'eau distillée afin d'éviter une évaporation à sec qui provoquerait la formation d'oxydes de fer hydratés difficiles à mettre en solution. On contrôle le départ du chlore au moyen de papier iodo-amidonné. Lorsque l'opération est terminée, on reprend par l'acide chlorhydrique concentré de telle sorte qu'on obtienne un volume de 10 à 15 ml.

Pour marquer cette solution, on introduit 2 ml de l'étalon cobalt 60 renfermé dans une éprouvette, dans le cristal creux et on en mesure l'activité totale. Ces deux ml sont ensuite introduits dans la solution chlorhydrique renfermant l'échantillon, puis on compte de nouveau l'activité de l'éprouvette vide pour en déterminer l'activité résiduelle. La différence de ces deux comptages donne l'activité de notre solution. Au début des opérations analytiques, on obtient avec l'étalon dont la composition est donnée ci-dessus, 10,000 à 12,000 c.p.m. Le cobalt 60 va jouer le rôle d'indicateur radioactif de pertes. Si on fait parallèlement une analyse avec étalon interne, on procédera de façon identique pour le marquage.

Extraction du fer

La quantité de fer est telle que celui-ci saturerait la résine dont la masse a été réduite autant que possible et le cobalt ne serait plus alors retenu quantitativement. Il faut donc éliminer la plus grande partie du fer par extraction. On transvase la solution dans une ampoule à décanter de 250 ml, on y ajoute 50 ml d'acide chlorhydrique 9 *N* et 40 ml d'éther saturé d'acide chlorhydrique concentré. Après agitation énergique pendant quelques minutes (l'équilibre entre les phases s'établit très rapidement lorsqu'on prend l'éther comme solvant organique), on laisse reposer 15 min, puis on sépare les phases. L'opération d'extraction est répétée trois fois; on élimine ainsi la plus grande partie du fer de la solution aqueuse. Si les opérations sont bien conduites la phase éther–HCl ne présente aucune activité; il n'y a donc pas de perte de cobalt au cours de ces opérations.

Séparation sur résine

La solution aqueuse verte qui résulte de l'extraction précédente et qui renferme le cobalt est chauffée à 60° au bain-marie pour éliminer l'éther qui y est dissous. Son volume est de 60 ml environ et la teneur en acide, qui convient bien à la séparation sur résine, n'a pas été modifiée par les opérations précédentes. Il faut en effet éviter toute variation de concentration en acide chlorhydrique, qui pourrait provoquer une rétention du nickel et du chrome sur la résine, le cobalt ne serait plus alors retenu quantitativement.

On fait donc passer la solution ci-dessus sur une colonne de 120 mm de hauteur et 8 mm de diamètre, ce qui correspond à un volume apparent de la résine Dowex I-X 8 (100/200 mesh) de 6 ml environ (celle-ci a été préalablement lavée avec 30 ml HCl 0.01 *N*, puis imprégnée de 10 ml HCl 9 *N*). La solution récupérée au bas de la colonne ainsi que les solutions acides de lavage ne doivent pas présenter d'activité notable. On perçoit, dans la partie supérieure de la résine, un anneau brun dû aux traces de fer, le cobalt se fixe immédiatement au-dessous. Quant au nickel et au chrome, ils traversent quantitativement la colonne. Le cobalt est élué par 30 ml d'une solution d'acide chlorhydrique 4 *N*. On reçoit, au bas de la colonne un liquide légèrement coloré en jaune vert qui renferme le cobalt et de petites quantités de résine, gênantes pour la détermination spectrophotométrique.

Élimination de la résine

On ajoute du citrate de sodium cristallisé à la solution, de telle sorte que la concentration soit de 10%. On porte au pH 8.2, tout d'abord par addition d'une solution concentrée d'hydroxyde de sodium en refroidissant, puis avec une solution normale d'hydroxyde de sodium. On transvase dans une ampoule à décanter de 200 ml et on extrait avec 5 ml d'une solution de 0.05% de dithizone dans l'éther. L'opération est répétée jusqu'à ce que la couleur de la solution éthérée ne change plus. On élimine ainsi les traces de résine. On termine par un lavage de cette dernière avec 5 ml d'éther pur et on mesure alors l'activité de la phase aqueuse, elle doit être négligeable.

Destruction de la dithizone

Les diverses solutions de dithizonate de cobalt dans l'éther ainsi que l'éther de lavage sont réunis dans une ampoule à décanter de 100 ml. On lave deux fois avec 2 ml d'acide chlorhydrique 0.1 *N* puis on transvase dans une capsule de pyrex et on ajoute 5 ml d'acide perchlorique. La capsule est recouverte d'un verre de montre creux renfermant un peu d'eau qui joue le rôle condensateur et on place le tout sur une plaque chauffante à 200°. Après deux heures environ, la dithizone est détruite quantitativement, la solution devient incolore. 5 ml d'une solution molaire de chlorure de potassium sont ajoutés, puis on évapore à sec et reprend par 1 ml d'acide chlorhydrique concentré, puis nouvelle évaporation à sec, nouvelle addition de 1 ml d'eau distillée, pour éliminer cette fois toute trace d'acide chlorhydrique. Le résidu de la capsule est repris par de l'eau distillée, ajoutée par petites fractions qu'on introduit dans un ballon de 5 ml jusqu'au trait de jauge.

Détermination spectrophotométrique

La solution est diluée, si nécessaire, de telle sorte qu'elle ne renferme pas plus de 2 à 3 μg/ml et pas moins de 0.01 μg/ml de cobalt. (Lorsque la teneur de cobalt dans l'acier est très faible, on ajoute après la destruction de la dithizone, 1 ml de la solution de chlorure de potassium au lieu de 5 ml. Le résidu, après élimination de l'acide chlorhydrique sera repris par 1 ml d'eau distillée).

Dans un tube à centrifuger de 5 ml, on introduit 1 ml de la solution précédente, 2 ml de tampon acétique de pH 6 (acétate de sodium à 10% additionné d'acide acétique glacial) et 0 5 ml d'une solution de nitroso-sel R à 0.05%. Le tube est placé une minute dans un bain-marie bouillant pour développer la coloration; puis on ajoute 0.5 ml d'acide nitrique concentré et on maintient au bain-marie 30 sec.

TABLEAU I

ANALYSE DU COBALT DANS L'ACIER PHOENIX MA 2 B

Analyse	*Prise (g)*	*Etalon interne (µg)*	*Activité avant (c.p.m.)*	*Activité après (c.p.m.)*	*Pertes (%)*	*Co trouvé (µg)*	*Co dans prise (%)*
1	0.5	—	11884	9734	18	225	0.045
2	0.5	—	12094	9561	21	210	0.042
3	0.1	—	11914	10126	15	44	0.044
4	0.1	—	11937	10407	16	42	0.042
5	0.1	—	11902	9758	18	41	0.041
6	0.1	—	12124	7271	40[a]	44	0.044
7	0.1	49.6	12014	9488	21	92	0.042
8	0.1	69.4	11987	8882	26	114	0.045
9	0.1	—	12342	10512	15	46	0.046
10	0.1	—	12385	10779	13	42	0.042
11	0.1	49.6	12332	9863	20	95	0.045
12	0.1	69.4	12455	10091	19	112	0.043
				Valeur moyenne			0.0434

[a] Cet écart n'est pas imputable aux séparations elles-mêmes, mais à une perte accidentelle.

Après refroidissement dans un courant d'eau, on complète au trait de jauge avec de l'eau bidistillée puis on centrifuge pendant 20 min pour rendre la solution optiquement vide. Cette dernière est introduite dans une cuve de 1 cm d'épaisseur et on mesure au spectrophotomètre Beckman la densité optique, à $\lambda = 520$ mμ, par rapport à un blanc, qu'on obtient en procédant exactement comme il a été fait pour l'échantillon.

Nous avons effectué une série de 12 dosages sur le même acier en partant de prises de 0.5 g et 0.1 g; les résultats sont donnés dans le Tableau I.

Les pertes ont été déterminées par la mesure des activités au début et à la fin de l'analyse.

Pour les analyses 7, 8, 11 et 12, une quantité connue de cobalt a été ajoutée au moment de la mise en solution de la prise (étalon interne), la marche du dosage étant par ailleurs identique.

En prenant les précautions nécessaires, il est possible de maintenir les pertes entre 15 et 20% et de les évaluer à, au moins, 5% près. Nous ne l'avons pas fait, car l'indicateur radioactif permet de les déterminer très exactement.

Étude statistique de la précision de la méthode

Elle a été faite sur les résultats des analyses 3 à 12, pour des prises de 0.1 g. L'écart type sur cette série de déterminations est de 0.485. Pour une probabilité de 95%, on aura un écart de ± 1.1 μg; le résultat est donc compris entre 41.9 et 44.1 μg, c'est-à-dire entre 0.0419 et 0.0441%.

MICRODOSAGE

La sensibilité de la méthode que nous avons mise au point permet d'effectuer les dosages du cobalt dans les aciers sur des prises beaucoup plus faibles que celles nécessaires au macrodosage. L'expérience nous a montré que les pertes ne sont proportionnellement pas plus grandes, par contre les opérations sont plus rapides. Pour des quantités d'échantillons comprises entre 1 mg et 10 mg, il n'est pas nécessaire d'effectuer une préextraction du fer à l'éther chlorhydrique, car il n'y a pas suffisamment de cet ion pour saturer la résine. En partant de 10 mg d'échantillon par exemple, le fer est fixé dans la moitié supérieure de la résine et le cobalt est retenu quantitativement sur celle-ci. Enfin, il suffit d'une seule extraction à la dithizone pour récupérer la totalité du cobalt.

Dans toutes les analyses que nous avons faites, il n'a pas été pris de précautions spéciales pour éviter les pertes au cours des diverses opérations analytiques, car celles-ci ont été déterminées par indicateur radiochimique. Des pertes allant jusqu'à 34% n'entachent pas la précision du dosage, comme on peut s'en rendre compte en examinant les résultats donnés dans le Tableau II.

Mode opératoire

Lorsqu'on effectue la détermination du cobalt par microdosage, certaines modifications et simplifications peuvent être apportées au mode opératoire donné précédemment.

En premier lieu, la mise en solution est beaucoup plus rapide; 5 ml d'eau régale sont suffisants pour l'effectuer. Pour les prises de 10 mg, le marquage se fait au moyen de 1 ml de la solution de cobalt actif dilué 10 fois; pour les prises de 1 mg, au moyen de 1 ml de la même solution diluée 100 fois. Après avoir chassé le chlore, on reprend par l'acide chlorhydrique 9 *N* de manière à obtenir un volume final d'environ 10 ml. Comme nous l'avons signalé plus haut, il est inutile de procéder à l'extraction du fer.

L'extraction par la dithizone en solution éthérée ne nécessite que 5 ml de réactif; elle est suivie de deux lavages à l'éther (5 ml).

La destruction du dithizonate au moyen d'acide perchlorique est plus rapide du fait de la faible quantité de réactif présent; une heure suffit en général pour obtenir une décoloration complète.

La reprise du résidu final, après minéralisation de la dithizone est faite au moyen de 2 ml d'eau bidistillée.

Les résultats obtenus sont donnés dans le Tableau II.

TABLEAU II

RÉSULTATS DE L'ANALYSE DE L'ACIER EDELWEISS "PHOENIX MA 2 B" SUR PRISES MICRO

Prises acier (mg)	*Co récupéré (%)*	*Densité optique*	*Co trouvé*[a] *(μg)*	*Co dans la prise (%)*
10	78.8	0.088	4.53	0.0453
10	89	0.0995	4.54	0.0454
10	75.3	0.085	4.58	0.0458
10	77.9	0.086	4.49	0.0449
			Valeur moyenne	0.0453
1	66	0.015	0.461	0.0461
1	90.5	0.020	0.449	0.0449
1	88.2	0.020	0.460	0.0460
			Valeur moyenne	0.0457

[a] Déduction faite du cobalt introduit comme traceur, soit 0.02 μg pour les prises de 10 mg et 0.002 μg pour les prises de 1 mg et corrections faites pour les pertes.

La quantité de cobalt introduite par le citrate (3 g) est de 0.015 μg. Il n'y a donc pratiquement pas de correction à apporter au résultat si l'on effectue des prises de 100 mg ou davantage.

Les résultats donnés sur les prises de 10 mg et de 1 mg doivent par contre tenir compte de ce facteur et l'on obtient finalement les valeurs suivantes:

Prises de 10 mg: 4.53 — 0.015 = 4.515 μg, ce qui donne une teneur de 0.0452% Co.

Prises de 1 mg — moyenne: 0.457 — 0.015 μg, teneur de 0.0442% Co.

DOSAGE POLAROGRAPHIQUE

(polarographe à rayons cathodiques)

Comme nous l'avons signalé par ailleurs, le dosage polarographique du cobalt est gêné par la présence de zinc même si celui-ci est en petites quantités. Il est introduit dans nos dosages par les acides nitrique et perchlorique nécessaires à la minéralisation du dithizonate. Les essais de purification de ces acides n'ont pas permis d'éliminer cet élément. Après distillation ils renferment autant de zinc sinon plus qu'avant et pourtant nous avons montré, au moyen de zinc 65, que l'ion initialement présent dans l'acide n'est pas entraîné lors de cette opération, le distillat ne présentant aucune radioactivité. Nous n'avons pas encore recherché les causes de cette contamination. Le mode opératoire a dû être quelque peu modifié pour éviter l'extraction à la dithizone. Lors de l'élution du cobalt fixé sur la résine Dowex, on prélève des fractions successives de 2 ml. Comme la solution initiale a été marquée au cobalt 60, l'activité de chacune de ces fractions est mesurée et l'on conserve pour le dosage celle qui est la plus riche en cobalt. Les ions de cet élément fixés sur la colonne restent groupés lors de l'élution de sorte qu'il est possible d'obtenir, dans une seule fraction de 2 ml, le 90% du cobalt total. La faible quantité de résine contenue dans un si petit volume ne gêne pas le dosage polarographique. Il est évident que seul le marquage au moyen d'un traceur radioactif permet de travailler de la manière décrite. Pour donner à la méthode toute la sûreté désirable, il est nécessaire de procéder à un étalonnage interne plutôt que de se référer à une courbe d'étalonnage. Pour cela, on conserve l'une des fractions d'éluat qui suit celle renfermant la quasi totalité de cobalt et qui ne présente plus d'activité. On y ajoute une quantité connue de cobalt (égale approximativement à celle renfermée dans l'échantillon). On effectue sur les deux fractions les mêmes opérations, ce qui permet de réduire les erreurs au minimum.

Marche de l'analyse

Les essais préliminaires nous ont montré que l'on n'obtient de résultats valables que si la quantité de cobalt est égale ou supérieure à 1 μg. Dans ces conditions, l'erreur est inférieure à 10%. Nous avons effectué les analyses sur des prises de 10 mg, les différents stades en sont: la mise en solution selon le processus décrit à la page 578, un marquage au cobalt 60, le passage sur colonne de résine Dowex dont les conditions sont données à la page 579. L'élution se fait au moyen d'acide chlorhydrique 4 *N* et l'éluat recueilli en fractions de 2 ml. Celle d'entre elles présentant l'activité maximum est retenue pour le dosage, une des suivante, d'activité nulle servira d'étalon externe; elle sera additionnée d'une quantité connue de cobalt. Ces deux fractions sont évaporées à sec, on y ajoute 1 ml d'une solution de chlorure de potassium 0.1 *N*; on évapore à sec, reprend par de l'eau distillée, évapore à sec une nouvelle fois pour chasser toute trace d'acide et reprend par deux à trois ml d'eau distillée. Après passage d'azote purifié pour chasser l'oxygène, on polarographie.

Les nombreux essais à blanc que nous avons faits ne donnent pas de saut au polarographe. Il n'y a donc pas de contamination au cours des opérations et les réactifs n'en renferment pas suffisamment pour gêner le dosage. Le Tableau III donne les principales valeurs obtenues.

C'est la valeur moyenne qui a permis de calculer les résultats donnés dans la sixième colonne.

Le dosage polarographique est moins sensible que le dosage spectrophotométrique, mais il donne de bons résultats lorsque la quantité de cobalt présente est suffisante. Il a l'avantage d'être plus simple et plus rapide.

TABLEAU III

Prise acier (mg)	*Activité ajoutée (c.p.m.)*	*Activité recueillie*		*Saut (μA)*	*Co trouvé μg*[a]	*Co dans la prise %*
		(c.p.m.)	%			
9.60	28,650	25,284	88.3	1.007	4.41	0.0459
9.60	28,650	25,240	88.1	1.027	4.51	0.0469
9.60	28,650	27,210	94.9	1.034	4.21	0.0438
9.60	28,650	24,928	87.0	0.980	4.34	0.0452

[a] Nous avons utilisé deux étalons; l'un donne un saut de 0.827 μA pour 3.20 μg de cobalt et l'autre 1.670 μA pour 6.40 μg.

TABLEAU IV

CARACTÉRISTIQUES DE NOS DIFFÉRENTES MÉTHODES APPLIQUÉES AU DOSAGE DU COBALT DANS UN ACIER 18/8

	Méthode spectrophotométrique		*Polarographie*	*Activation avec étalon interne*
	macro	*micro*		
Poids des échantillons	100 mg	1 mg	10 mg	1 à 5 mg
Effets — des pertes	nul	nul	nul	nul
— des contaminations	corrigé par un blanc		corrigé par un blanc	nul
Principales causes d'erreurs	coloration du réactif, mesure de D		mesure de la vague en présence d'impuretés	mesure du pic du cobalt 58
Ordre de grandeur des erreurs	4%	8%	6%	5%
Indicateur radioactif	nécessaire	nécessaire	nécessaire	inutile
Dosage: limite absolue	0.02 µg	0.005 µg	0.1 µg	0.2 µg
Dosage: limite relative	0.01 µg/ml	0.01 µg/ml	0.5 µg/ml	—
Résultats	0.043%	0.045%	0.045%	0.049%

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RÉSUMÉ

Il est proposé une méthode de dosage spectrophotométrique permettant de déterminer la concentration de cobalt dans un acier 18/8, sur 0.1 à 0.5 g pour le macrodosage et sur 1 mg pour le microdosage; les erreurs sont comprises entre 4 et 6%. La méthode consiste à extraire le fer, à séparer le cobalt sur résine Dowex 1-X 8 et à déterminer la densité optique du complexe cobalt-nitroso-sel R. La limite de sensibilité du dosage est de 0.01 µg/ml. Le microdosage se fait en microcuve avec un photomultiplicateur; il permet de doser encore 0.005 µg de cobalt. Il est aussi proposé une méthode polarographique moins sensible (0.5 µg/ml) mais plus rapide. Les erreurs sont du même ordre de grandeur.

SUMMARY

A spectrophotometric method for the determination of cobalt in 18/8 steel is described. Iron is removed by solvent extraction, cobalt is separated by means of an ion-exchange resin and converted to the nitroso-R-salt complex, the optical density of which is then measured. The method can be applied on the macro- and on the micro-scale. The limit of error lies between 4 and 6%; the limit of identification is 0.005 µg cobalt. A less sensitive (0.5 µg/ml) but more rapid polarographic method is also described.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Kobalt in 18/8 Stahl. Eisen wird durch Lösungsmittel-Extraktion entfernt, das Kobalt mit einem Austauscherharz abgetrennt und in den Nitroso-R-Salz Komplex übergeführt, dessen optische Dichte dann gemessen wird. Das Verfahren kann als Makro- und Mikromethode angewandt werden. Die Fehlergrenze liegt zwischen 4 und 6%. Erfassungsgrenze: 0.005 µg Kobalt. Ferner wird eine weniger empfindliche (0.5 µg/ml), aber raschere polarographische Methode beschrieben.

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CURRENT–TIME CHARACTERISTICS OF THE RAPIDLY DROPPING MERCURY ELECTRODE

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Dropping mercury electrodes (DME) with short drop times have been considered unsuitable as indicator electrode in polarography because of the presence of the maximum of the second kind owing to the "Spüleffekt"[1]; only a few papers on such an electrode have been published[2]. KOONS studied the properties of the DME with a normal rate of mercury flow but a very short drop time under the high pressure applied to the electrode[3]. Recently, KARCHMER carried out a systematic investigation on DMEs with a short drop time and used the electrode for the polarographic determination of dissolved oxygen in natural and effluent waters[4]. In previous papers[5,6], the present authors have pointed out that the rapidly dropping mercury electrode (RADME), whose drop time is less than 1 sec, seems to be one of the most suitable indicator electrodes in alternating current (a.c.) polarography. It was also shown in direct current (d.c.) polarography that, in the presence of a sufficient amount of surface-active substances (SAS), the maximum of the second kind seems to be completely suppressed and current–voltage curves similar to those at the conventional DME are observed at the RADME[6]. In this paper, the characteristics of the RADME in stationary and flowing media are investigated by measurements of the current–time curves during the life of a mercury drop.

REAGENTS AND APPARATUS

The standard solution of mercury(II) was prepared by dissolving a known amount of purified mercury metal in concentrated nitric acid. The standard solutions of lead nitrate and cadmium nitrate were prepared from guaranteed grade reagents and standardized amperometrically against standard ethylenediaminetetraacetate solution[7]. Polyoxyethylene lauryl ether (LEO) was obtained from Nikko Co., Tokyo ("Nikkol BL-10"). All other chemicals used were of analytical reagent grade. Redistilled water was used for the preparation of the solutions.

Current–voltage curves were recorded with a Yanagimoto Y-GR Model 2 Galvarecorder (pen-recording polarograph) or measured with a manual apparatus similar to that of KOLTHOFF AND LINGANE[8]. In the measurement of current–time curves, the ohmic potential drop (less than 2 mV) across the standard variable resistance R (Fig. 1) was amplified by the d.c. amplifier (Fig. 2) and recorded with the mechanical oscillograph (N-6 type of Yokogawa Electric Works Co.). The characteristics of the conventional DME and the RADME used in the present study are shown in Table I. A saturated calomel electrode of large surface area was used as the anode, and was connected to the electrolytic solution by a Hume and Harris-type agar bridge[9]. All measurements in stationary media were made in a thermostat at 25.0 ± 0.1°. The dissolved oxygen in the solution was expelled by passing pure nitrogen gas. The current–voltage and current–time curves presented in this paper are corrected for residual currents.

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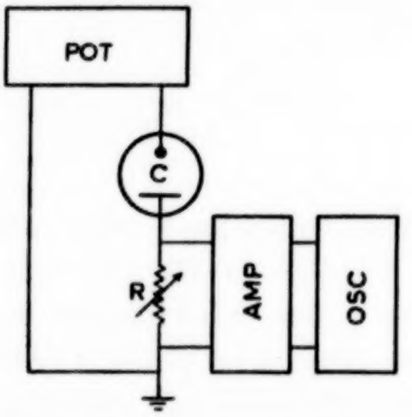

Fig. 1. Circuit for the measurement of current–time curves: POT, applying potentiometer; C, electrolysis cell; R, standard variable resistance; AMP, d.c. amplifier; OSC, mechanical oscillograph.

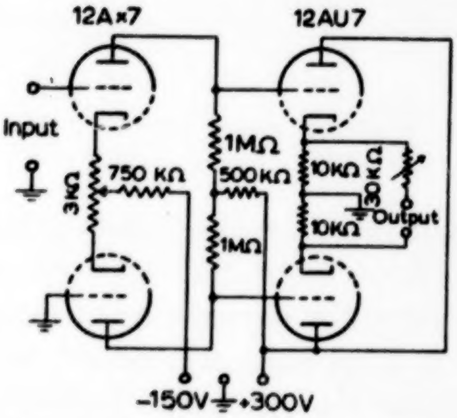

Fig. 2. Circuit of the d.c. amplifier.

TABLE I

CHARACTERISTICS OF THE CONVENTIONAL DME AND THE RADME

Electrode	*Rate of flow of mercury* m, *mg/sec*	*Drop time* τ, *sec*
DME[a]	2.43_8	3.68_9
RADME[b]	20.4_3	0.67_0

[a] Measured in an air-free 0.1 M KCl–0.005% gelatin solution; open circuit; height of the mercury column, 45 cm

[b] Measured in an air-free 0.1 M HNO_3 solution; open circuit; height of the mercury column, 50 cm

All experiments in the flowing media were carried out in a thermostat of 25 ± 1° with the electrolysis cell as shown in Fig. 3. The flow rate of the solution was varied by changing the speed of rotation of stirrer S which was rotated by a synchronous motor. Preliminary experiments showed that the current–voltage curves in flowing media were not affected appreciably by a slight change in the position of the tip of the RADME.

RESULTS

One of the examples which show the effect of polyoxyethylene lauryl ether (LEO) on the current–voltage curves observed at the RADME in stationary media is shown in Fig. 4. Fig. 5 presents the current–time curves of cadmium(II) which were obtained with the RADME in stationary 0.1 M potassium nitrate solutions in the presence and the absence of LEO. The plots of log i vs. log t of those current–time curves are given in Fig. 6. Similar results were also obtained with lead(II) in 0.1 *M* potassium nitrate solutions and with mercury(II) in 0.1 *M* nitric acid solutions.

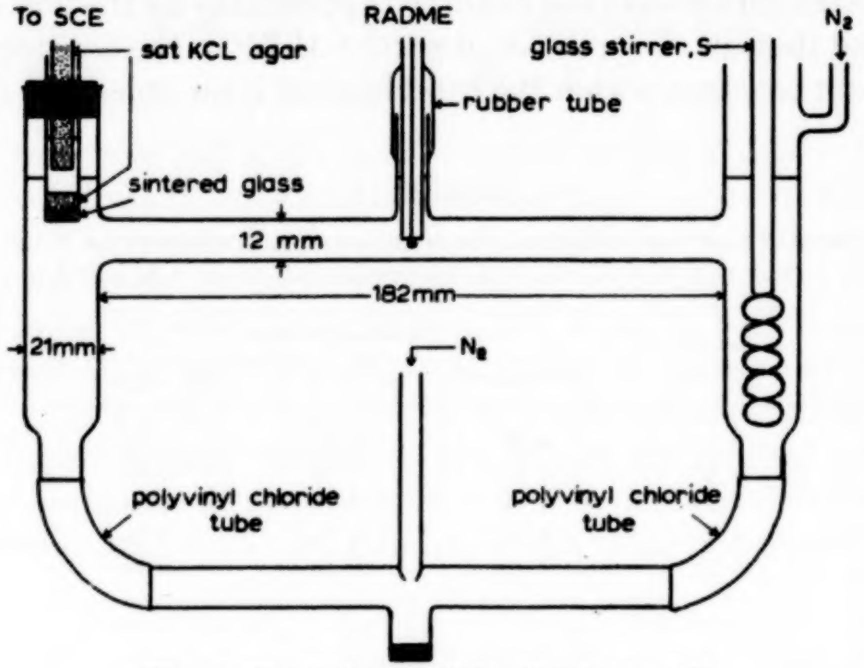
To SCE
RADME
glass stirrer, S
N_2
sat KCL agar
rubber tube
sintered glass
12 mm
182mm
21mm
N_2
polyvinyl chloride tube
polyvinyl chloride tube

Fig. 3. Electrolysis cell for flowing media.

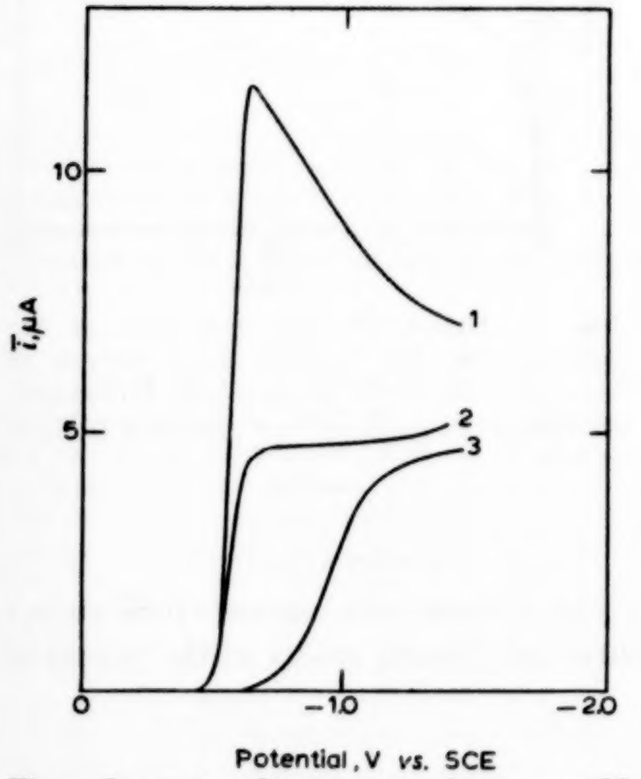

Fig. 4. Current–voltage curves of $2.00 \cdot 10^{-4}$ *M* $Cd(NO_3)_2$ in 0.1 *M* KNO_3 in the absence and in the presence of LEO. Concentration of LEO: (1) 0; (2) $5 \cdot 10^{-5}$ *M*; (3) $5 \cdot 10^{-4}$ *M*.

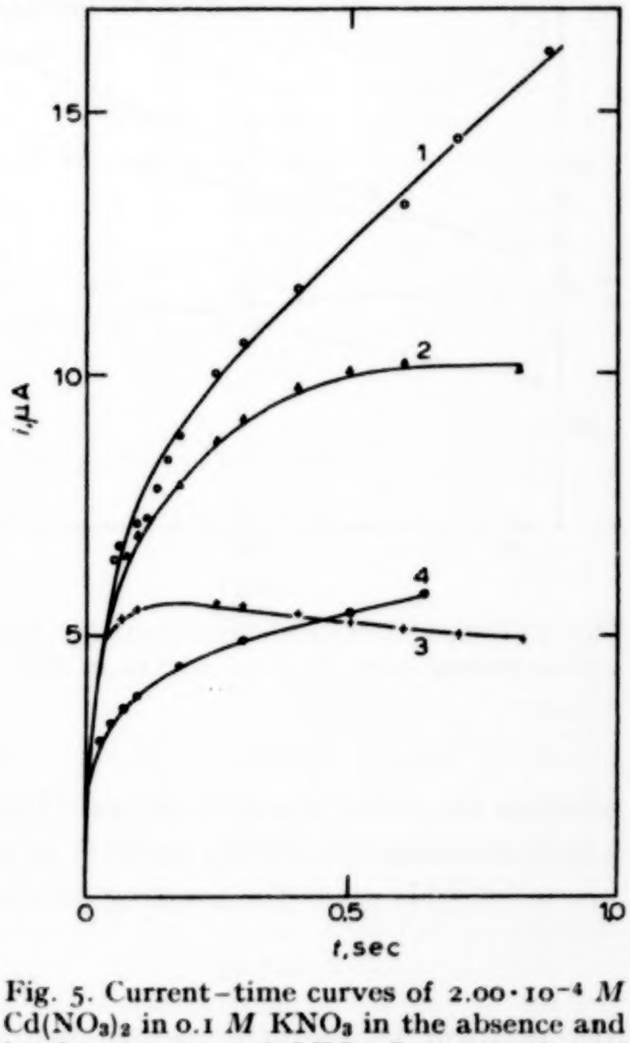

Fig. 5. Current–time curves of $2.00 \cdot 10^{-4}$ *M* $Cd(NO_3)_2$ in 0.1 *M* KNO_3 in the absence and in the presence of LEO. Concentration of LEO: (1) 0 (—0.65); (2) 0 (—1.00); (3) $5 \cdot 10^{-5}$ *M* (—1.00); (4) $5 \cdot 10^{-4}$ *M* (—1.4). The values in parentheses are the electrode potentials in V *vs.* SCE where the current–time curves are measured.

The effect of the flow of the solution on the current–voltage and current–time curves was investigated in 0.1 M potassium nitrate solutions of lead(II). In general, the current–voltage curves were not disturbed appreciably by the flow of the solution. It was also found that, in the presence of $5 \cdot 10^{-4}$ M LEO, the limiting current at the RADME was kept constant within the experimental error unless the flow rate of the solution exceeded about 3 cm/sec (Table II). Fig. 7 shows the current–time curves which were obtained with lead(II) in stationary and flowing media at the potential where lead(II) gives the limiting current.

TABLE II

EFFECT OF THE FLOW RATE OF THE SOLUTION ON THE LIMITING CURRENT OF $2.14 \cdot 10^{-4}$ M $Pb(NO_3)_2$ IN 0.1 M KNO_3 SOLUTION CONTAINING $5 \cdot 10^{-4}$ M LEO

Flow rate, cm/sec	*Limiting current*		
	at −0.80 V	*at −1.00 V*	*at −1.40 V*
0	4.8_0	4.8_0	4.6_5
0.5_7	4.7_7	4.8_0	4.6_2
1.7_9	4.7_8	4.7_6	4.5_4
3.2_5	4.7_8	4.7_4	4.6_0
8.9_4	6.3_9	6.4_4	6.2_7

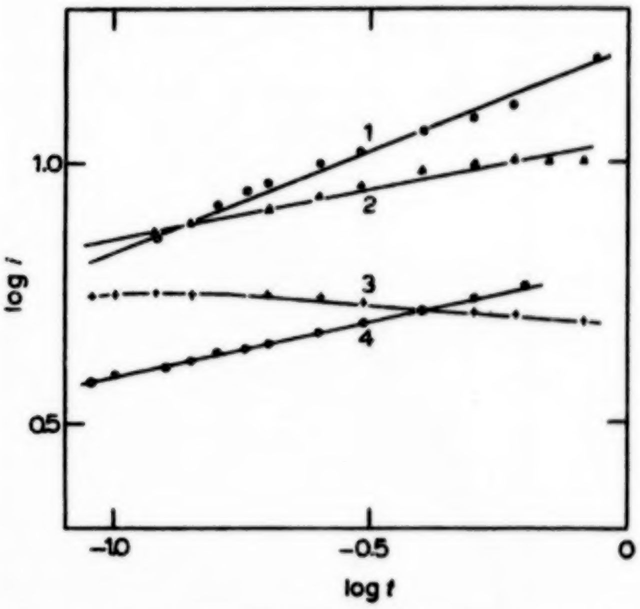

Fig. 6. Relations between log i and log t of the corresponding current–time curves in Fig. 5.

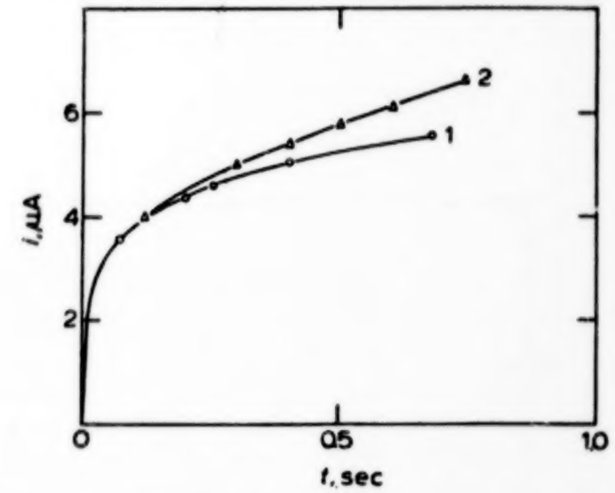

Fig. 7. Effect of the flow rate of the solution on the current–time curves of $2.14 \cdot 10^{-4}$ M $Pb(NO_3)_2$ in 0.1 M KNO_3 containing $5 \cdot 10^{-4}$ M LEO at the potential of −0.80 V *vs.* SCE. Flow rate: (1) 0; (2) 1.8 cm/sec.

DISCUSSION

The relation between the instantaneous current i and the time t during the life of a drop of the DME is generally considered to be represented by the equation:

$$i = kt^x \tag{1}$$

where k and x are the constants determined by the nature of the mass-transfer process.

From eqn. (1) the average current $\bar{i}$ during the life of a drop is expressed by the relation,

$$\bar{i} = \frac{1}{\tau} \int_0^\tau i \, dt = \frac{1}{1 + x} i_\tau \tag{2}$$

where τ is the drop time and i_τ the instantaneous current at $t = \tau$. If the current is controlled by the diffusion, the value of x should be equal to 0.167 according to the Ilkovic equation. This prediction has been examined by many investigators[10], and the value of x of the diffusion-controlled limiting current observed at the conventional DME has been found experimentally to be nearly equal to 0.2 except for the initial part of the current–time curve. On the other hand, if the current is controlled by the convection, the value of x is expected to be 0.5 from theoretical considerations[11]. This has been experimentally verified in the case of the limiting current obtained with the rotated dropping mercury electrode[11,12]. Therefore, if the current is controlled by both diffusion and convection, the value of x must be between 0.167 and 0.5.

TABLE III

CHARACTERISTICS OF THE LIMITING CURRENTS WITH THE RADME IN THE ABSENCE OF SAS

Ionic species:	*Hg(II)*[a]			*Pb(II)*[b]		*Cd(II)*[c]	
Electrode potential, V vs. SCE:	*0*	*−0.50*	*−0.80*	*−0.45*	*−1.00*	*−0.65*	*−1.00*
x	0.21_5	0.31_7	0.28_6	[d]	0.16_0	0.35_3	0.23_7
$1/(1 + x)$	0.82_3	0.76_0	0.77_8	[d]	0.86_2	0.73_9	0.80_8
$\bar{i}/i_\tau$	0.82_4	0.74_3	0.78_3	[d]	0.88_3	0.70_7	0.89_1

[a] $2.10 \cdot 10^{-4}$ M $Hg(NO_3)_2$ – 0.1 M HNO_3.
[b] $2.00 \cdot 10^{-4}$ M $Pb(NO_3)_2$ – 0.1 M KNO_3.
[c] $2.00 \cdot 10^{-4}$ M $Cd(NO_3)_2$ – 0.1 M KNO_3.
[d] Cannot be determined because of the anomalies of the current–time curves.

TABLE IV

CHARACTERISTICS OF THE LIMITING CURRENTS OBTAINED WITH THE RADME IN THE PRESENCE OF $5 \cdot 10^{-4}$ M LEO

Ionic species:	*Hg(II)*[a]			*Pb(II)*[b]		*Cd(II)*[c]
Electrode potential, V vs. SCE:	*0*	*−0.50*	*−0.80*	*−0.80*	*−1.00*	*−1.40*
x	0.24_1	0.20_7	0.21_7	0.19_7 (0.23_6)	0.19_4	0.21_1
$1/(1 + x)$	0.80_6	0.82_9	0.82_2	0.83_7 (0.80_9)	0.83_8	0.82_5
$\bar{i}/i_\tau$	0.79_6	0.81_9	0.78_1	0.82_6 (0.77_5)	0.82_0	0.82_9

[a] $2.10 \cdot 10^{-4}$ M $Hg(NO_3)_2$ – 0.1 M HNO_3 – $5 \cdot 10^{-4}$ M LEO.
[b] $2.00 \cdot 10^{-4}$ M $Pb(NO_3)_2$ – 0.1 M KNO_3 – $5 \cdot 10^{-4}$ M LEO.
[c] $2.00 \cdot 10^{-4}$ M $Cd(NO_3)_2$ – 0.1 M KNO_3 – $5 \cdot 10^{-4}$ M LEO.
Values in parentheses are those obtained in flowing media (flow rate, 1.8 cm/sec).

The results of the analysis of the current–time curves which were obtained with the RADME under various conditions are summarized in Tables III and IV. The average current was determined by the graphical integration of the current–time curve. In the absence of LEO, the value of x at potentials near the electrocapillary maximum, where the maximum of the second kind is the most pronounced, is usually larger than 0.3, as shown in Table III. This means that the current under these conditions is controlled by diffusion as well as by convection due to the "Spüleffekt". On the other hand, Table IV shows that the values of x of the limiting current obtained with the RADME in the solutions containing $5 \cdot 10^{-4}$ M LEO are between 0.19 and 0.25 in all cases. This indicates that, in the presence of a sufficient amount of SAS, the "Spüleffekt" is completely eliminated and the limiting current at the RADME is mainly controlled by the diffusion. It must be mentioned here that, in the presence of $5 \cdot 10^{-5}$ M LEO, no maximum of the second kind appears on the current–voltage curve (Fig. 4), while the current–time curve (Fig. 5(3)) clearly shows the effect of convection on the limiting current.

It is very interesting that the limiting current at the RADME is independent of the flow rate of the solution within a certain range (Table II). The results of the current–time curves (Fig. 7 and Table IV) also indicate that the limiting current observed at the RADME in the presence of a sufficient amount of SAS is not affected appreciably by the flow of the solution. Similar results have been reported by KARCHMER with the limiting current of oxygen in the potassium chloride solutions[4]. These facts may be explained in the following way. The thickness of the diffusion layer at the surface of the DME is proportional to the square-root of time[13]. Therefore, the thickness of the diffusion layer established during the life of a mercury drop is thinner at the RADME than at the conventional DME, and the current at the RADME is less sensitive to the movement of the bulk solution.

From the experimental results mentioned above, it is concluded that the characteristics of the limiting current at the RADME in the presence of a sufficient amount of SAS, *e.g.* $5 \cdot 10^{-4}$ M LEO, are similar to those at the conventional DME. The fact that the limiting current obtained with the RADME is not affected appreciably by the flow of the solution unless the flow velocity exceeds a certain critical value suggests that the RADME is a suitable indicator electrode in d.c. polarography in flowing media.

ACKNOWLEDGEMENT

The authors thank Dr. M. MATSUO, Tohoku University, for his kind advice in constructing the direct current amplifier. They also thank the Ministry of Education for the financial support granted for this research.

SUMMARY

The properties of the rapidly dropping mercury electrode (RADME) in stationary and flowing media were studied by measurement of the current–time curve during a drop-life. In the absence of surface-active substance (SAS), the limiting current observed at the RADME in the potential region where the maximum of the second kind appears, was shown to be controlled by both diffusion and convection. However, in the presence of a sufficient amount of SAS, the maximum of the second kind was completely suppressed and the characteristics of the limiting current at the RADME were similar to those at the conventional DME. It was also shown that the limiting current of lead(II) obtained with the RADME in 0.1 M potassium nitrate solutions containing $5 \cdot 10^{-4}$ M polyoxyethylene lauryl ether was almost independent of changes in flow rate of the solution up to about 3 cm/sec. These results suggest that the RADME is a suitable indicator electrode in d.c. polarography in flowing media.

RÉSUMÉ

Une étude a été effectuée sur les caractéristiques de l'électrode à gouttes de mercure rapide, dans divers milieux. Les résultats obtenus montrent qu'une telle électrode peut être utilisée comme électrode indicatrice en polarographie à courant continu ("flowing media").

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Eigenschaften der schnell-tropfenden Quecksilberelektrode in stationärem und fliessendem Medium. Die Ergebnisse zeigen, dass diese Elektrode als Indikatorelektrode bei der Gleichstrom-polarographie mit fliessendem Medium verwendet werden kann.

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BOOK REVIEWS

Modern methods of analysis of copper and its alloys, by Charles M. Dozinel, translated by George R. Andraso, Georges Thone, Liège, 1960, 239 pp., price $ 32.00.

The important position occupied by the copper industry has made it necessary to analyse a great number of copper-containing materials. Consequently there has been a great increase in the scientific literature on this subject during the last ten years. When performing such analyses it is in many cases necessary to make a prolonged and laborious study of the original papers in order to obtain the necessary information concerning the most reliable method.

This book is designed to overcome this difficulty to a certain extent by providing a compact source for the widely spread information. Unpublished laboratory reports as well as scientific journals have been consulted in compiling this summary. Some procedures that seemed doubtful have been tested to ensure reliability. For more than twenty elements that can be present in copper alloys, the existing modern analytical methods in the field of gravimetry, titrimetry, electrolysis, polarography, and colorimetry, as well as combined procedures are reviewed. Some reliable procedures are treated more extensively so that in these cases the original papers need not be consulted. At the beginning, two separate chapters are devoted to a survey of the spectrographic methods — emission, X-ray and mass spectrography — and to practical data on qualitative and quantitative chemical wet methods. Finally some general considerations are devoted to important problems in connection with industrial analysis, mainly concerning rationalization.

The bibliography contains 767 references. Some more or less important procedures and books concerning the five chemical methods discussed have, however, been overlooked, and the references are not always given in the same way. Also new methods such as radiochemistry, which is already being used to determine traces of metals in copper alloys, are not discussed.

The price of the book is rather high when compared with that of other similar publications, but as far as research and consulting the literature are concerned, industrial laboratories will be able to save much time by using this work.

F. Verbeek (Ghent)

Anal. Chim. Acta, 23 (1960) 591–592

X-Ray Absorption and Emission in Analytical Chemistry, Spectro-chemical Analysis with X-Rays, H. A. Liebhafsky, H. G. Pfeiffer, E. H. Winslow et P. D. Zemany, John Wiley, New York, 1960, 357 pages, Prix $ 13.50.

Les méthodes d'analyses physico-chimiques se multiplient. La plupart d'entre elles sont remarquables, tant par la sensibilité que par la rapidité des dosages. Elles font appel aux chapitres les plus divers de la physique moderne, aussi le chimiste est-il souvent fort embarrassé lorsqu'il doit faire un choix. Il n'est pas facile de se familiariser avec des méthodes si spéciales et de se rendre compte des possibilités qu'elles offrent tant en ce qui concerne la nature des substances qu'il est possible de doser que les conditions dans lesquelles s'effectuent la détermination et la précision des résultats.

Heureusement que certains spécialistes de ces questions tels que ceux qui ont conçu cet ouvrage, effectuent le travail de synthèse, d'épuration grâce auquel des sujets aussi complexes que ceux de l'utilisation des rayons X pour l'identification et le dosage sont mis à la portée de l'analyste, lui permettant de se faire rapidement une idée du problème.

L'ouvrage de Liebhafsky *et coll.* répond très exactement à ce qu'on attend de lui; il donne une vue d'ensemble du problème, sans vains bavardages, sans démonstrations inutiles. Au lecteur de faire son choix, d'étudier le chapitre qui le concerne. Le style en est concis, l'exposé clair et bien ordonné. Peut-être les auteurs auraient-ils pu dresser une liste des abréviations et des symboles utilisés avec leurs définitions exactes.

Dans un premier chapitre intitulé origine et propriétés des rayons X, le lecteur s'initie sans grandes difficultés aux principes de bases sur lesquels reposent les analyses. Les chapitres suivants traitent des mesures de l'intensité des rayons X, de l'absorptiométrie, des rayons poly- et monochromatiques, de la détermination des épaisseurs, de la spectrographie d'émission des rayons X, de l'équipement et de la reproductibilité. Tout le problème a été pensé en analyste, des exemples sont donnés, tels que le dosage des métaux dans les minerais, du fluide tétraéthyle dans les essences, du chlore dans les plastiques. Un chapitre est consacré au dosage de traces. Il est encore possible de doser, par cette méthode, des quantités de l'ordre de μg. Des appendices terminent l'ouvrage, qui donnent les valeurs de l'absorption critique, des intensités des raies X, de leurs longueurs d'onde caractéristiques, etc.

Présentation parfaite, dessins, figures et photographies très soignés.

D. Monnier (Genève)

Anal. Chim. Acta, 23 (1960) 592

Analytical Chemistry of Titanium Metals and Compounds by Maurice Codell, Interscience, New York, 1959, 378 + xiii pp., price $ 12.00.

Although analytical procedures for the examination of titanium-bearing minerals and titanium-based pigments have been available for more than twenty years, it is only comparatively recently that the metal titanium has become commercially important and analytical methods for its examination have become available. With rapid advances in metallurgical methods of extraction, melting and fabrication of the metal, production of titanium has increased considerably and this has added to the importance of this relatively new analytical field.

There is little doubt that by bringing together, into a single volume, published information on this subject, Dr. Codell has made a useful contribution to analytical chemistry and enhanced the value of his book by drawing widely on information afforded by unpublished American reports.

The technical standard of this publication is generally high, but a major criticism is that almost

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without exception the recommended methods are of American origin and a more cosmopolitan approach to the subject is justified, particularly when so much information on the subject has been published elsewhere.

Part I contains chapters on the general chemistry of the subject; sampling, dissolution, general methods of separation, emission spectrographic procedures, vacuum line methods and methods determining titanium. The section on vacuum methods is particularly informative and the relatively complicated apparatus well illustrated.

In Part II methods are detailed for determining more than twenty metals in titanium and its alloys, and for most of these, several procedures are given, thus providing for the determination of trace and alloying amounts of the elements in question. At the beginning of each procedure the chemical principles involved are briefly discussed, and elements which interfere in specified determinations are enumerated; the work is, therefore, by no means merely a manual of laboratory methods. The uses and limitations of each procedure are also indicated, thus affording a useful guide to the analyst in his choice of method. The procedures described are generally based on well established principles, and it is note-worthy that use has been made of analytical methods involving polarographic and ion-exchange principles. There is little in this particular section to arouse adverse comment, but it is surprising to find that no reference is made to volumetric methods for determining aluminium. For instance, following precipitation of aluminium oxinate (p. 110), it is more expedient, and just as reliable, to complete this determination by titration using a standard solution of potassium bromate/bromide than by the recommended gravimetric method. In some instances a complexometric titration might be used to advantage, *e.g.* in the determination of aluminium (p. 108) and nickel (p. 198).

Part III of the book covers the determination of non-metallics in titanium and its alloys and includes methods for determining hydrogen, carbon, silicon, nitrogen, phosphorus, boron oxygen, and chlorine, and, as in the earlier sections of the book, each procedure is prefaced by an informative discussion which reflects the high standard of the methods described. In the hydrogen determination, however, difficulties associated with obtaining satisfactory blank values and with oxidising large (10 g) samples of titanium, are not emphasised. The range of this determination is stated on page 238 as 0.001 to 0.1% hydrogen, but the method described, would generally be considered suitable only for hydrogen contents greater than about 0.005%.

In the final section (Part IV) the analysis of titanium-base materials, including titanium tetrachloride, pigments, minerals and ores, is very well covered and presumably these procedures are in current use in the pigments department of E.I. Dupont de Nemours. The methods are based on sound analytical principles and the high technical standard and clarity of presentation are present in this section also. The book is remarkably free from obvious typographical errors, although on two separate occasions (pp. 308 and 310) lithopone is spelled incorrectly, and in the same section the composition of lithopone is twice referred to as $ZnS-PbSO_4$.

There is no doubt that this book will be useful to all concerned with the analysis of titanium-bearing materials, and it can be regarded as a worthy contribution in the field of analytical chemistry.

D. F. Wood (Birmingham)